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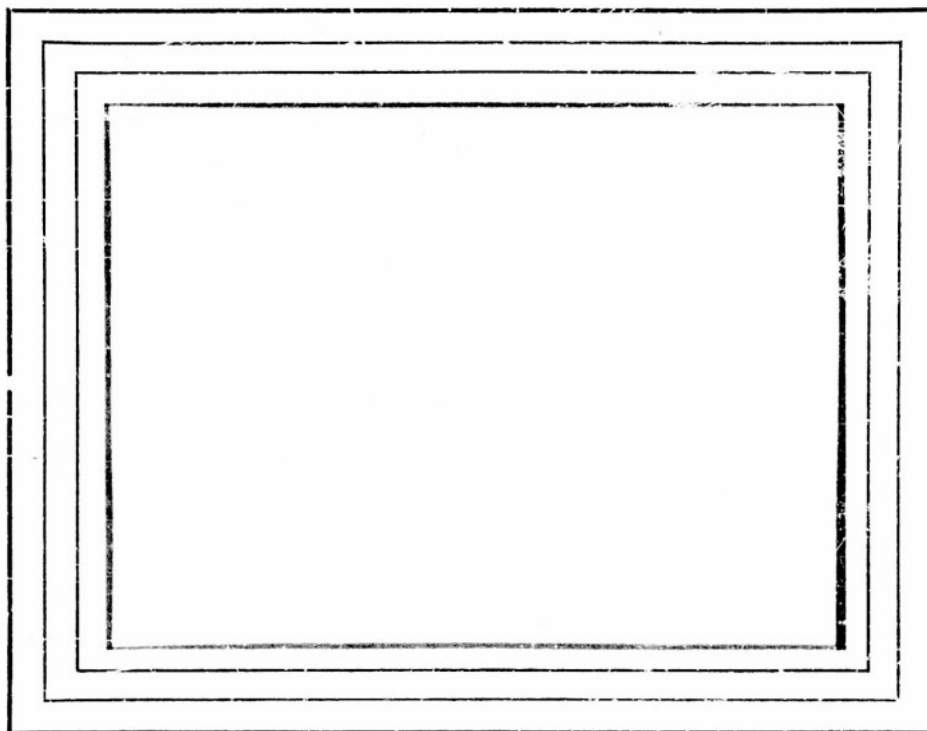
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FINAL REPORT

Investigations of Secondary  
Electron Emission

Contract Nonr-193(00)

Period - Nov. 1, 1950 - Feb. 1, 1954

Office of Naval Research

Electronics Branch

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## ABSTRACT

A detailed examination and critical evaluation of the existing theories of secondary electron emission has been conducted.

Among the new theoretical approaches which were considered was the application of the method of virtual quanta which had been employed successfully in studies of the interaction of high energy electrons with matter. Although the results obtained were in good agreement with experimental results, and the method of virtual quanta predicts the observed universal energy-dependence curve, detailed investigation of the conditions for validity revealed that the method cannot be utilized in its exact form in the solution of the present problem.

Calculations have indicated that the bulk of the secondaries originate in the bound states in most metals.

The principal conclusions based upon the results of an investigation of the interaction between the primary and conduction electrons are that the Wooldridge theory of secondary emission is in error, and that the correct expression for the rate of production of internal secondaries is very similar in form to that obtained by Bethe for the ionization of gases.

An expression for the energy-dependence of high-energy secondary emission has been derived, and on the basis of certain assumptions regarding the escape probability, the influence of primary scattering on low energy secondary emission has been demonstrated.

### ABSTRACT (Continued)

The experimental program has been directed toward the study of secondary emission under conditions such that the primaries pass through the target without appreciable energy loss. Targets ranging over the periodic system from carbon to gold, as thin as  $5 \times 10^{-6}$  inches and as thick as  $10^{-2}$  inches, have been bombarded with a 1.3 Mev beam provided by the Bartol linear accelerator. A new technique which permits measuring the yield from both faces of a thin target has been developed. The forward-backward ratio for an 11 mg cm<sup>-2</sup> Ni target is  $\delta_2 / \delta_1 = 1.02 \pm 0.05$ .

The emission of energetic secondary electrons (delta rays or knockon electrons) has been investigated. There is only a small dependence of the yield upon target material for an equivalent thickness expressed in mg cm<sup>-2</sup>. For 45.8 mg cm<sup>-2</sup> Ni, the delta-ray yield is  $2.08 \pm 0.15$  percent, as compared with  $1.48 \pm 0.25$  percent, the yield of low-energy secondaries from the same surface. The dependence of the yield upon target thickness and material is in accord with the results of a theoretical analysis of the phenomenon.

## I. INTRODUCTION

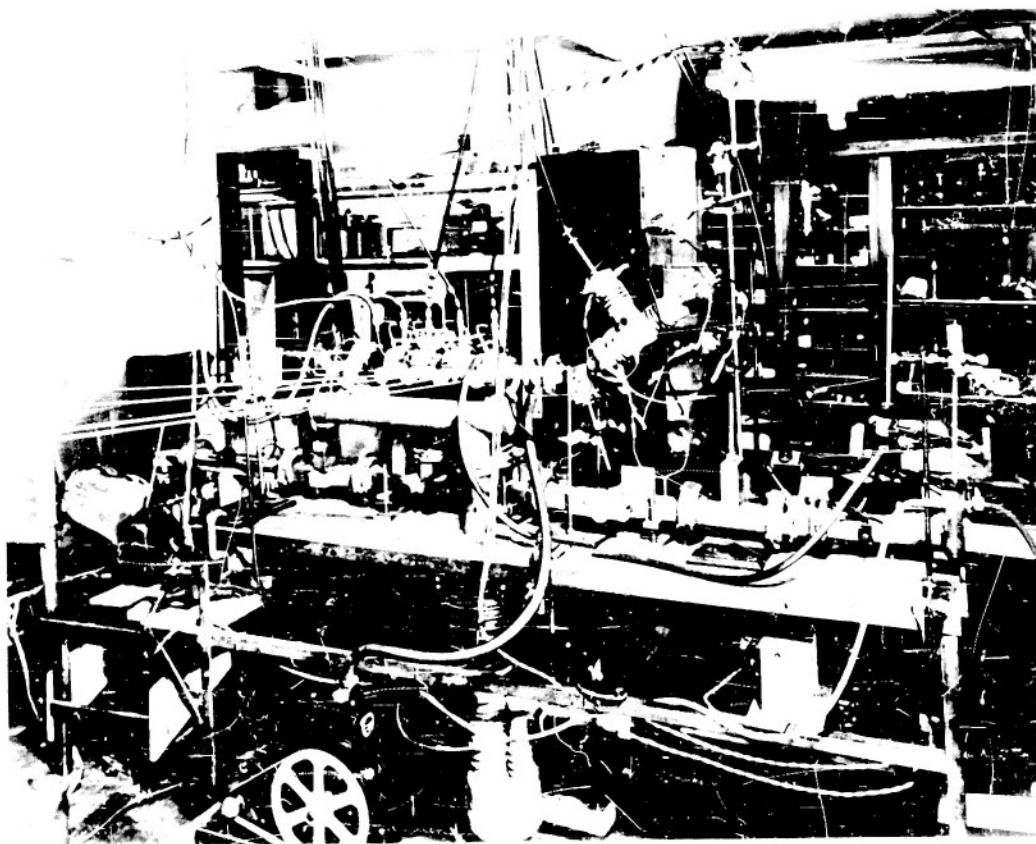
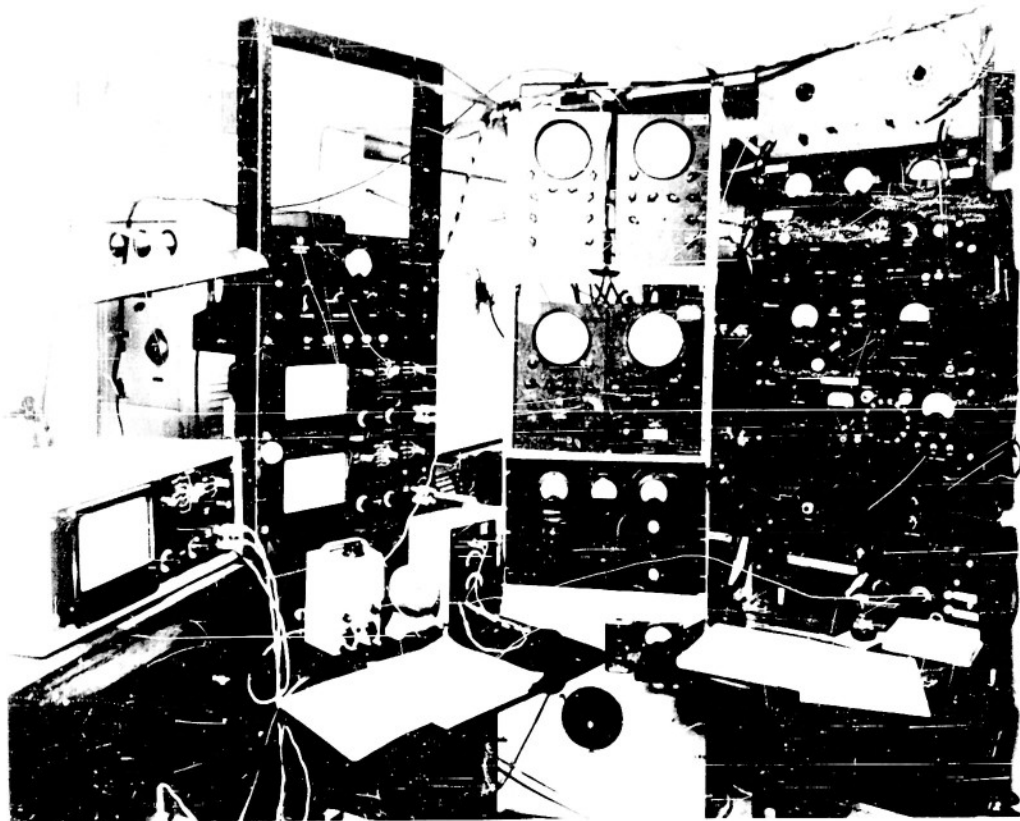
The present program of investigations of secondary electron emission was initiated in November, 1950, under the sponsorship of the Office of Naval Research. Attention was confined initially to a theoretical study of various aspects of this general subject, with the aim ultimately of performing such experiments as might appear crucial from the point of view of testing specific theoretical predictions in the absence of satisfactory existing data. A primary mission of this project was to conduct a critical survey of the entire field, in order to determine what line of attack, if any, would be fruitful in the endeavor to advance our understanding of this extremely complex phenomenon.

Various approaches to this problem have been explored, and the principal conclusions which have emerged either from general or detailed considerations are summarized in this final report.

It was apparent at the outset that measurements obtained by bombarding, with very high energy primary electrons, targets which are sufficiently thin to permit the impinging electrons to pass through with negligible scattering and energy loss would render certain phases of the process of secondary electron emission more susceptible to theoretical treatment. Consequently, at the beginning of the second year of operation of this contract, a program of experiments was undertaken utilizing the Bartol multiple-cavity linear accelerator as the source of a 1.3 Mev electron beam. The existence of this device, which had been developed and constructed in this laboratory as part of the nuclear physics program sponsored by the Office of Naval Research under Contract N6ori-1144, was indeed a very fortunate circumstance from the point of view of the secondary

**Fig. 1**

- (A) Control console of Bartol linear accelerator.
- (B) Four-cavity linear accelerator and associated equipment. The cavities are tuned by means of the rods which extend into the control room. The demountable experimental tube utilized in the investigations of secondary electron emission is attached to the magnetic spectrum analyser at the output end of the machine. The maximum attainable energy is approximately 1.5 Mev.



electron emission investigations. It soon became evident that the linear accelerator could profitably be devoted almost exclusively to solid state and physical electronics problems, and that its continued operation as well as further developments, such as the extension to higher energies, should be promoted as an independent project. In accordance with this policy, since February 2, 1953, the experimental program has been continued with the support of the Office of Ordnance Research, under Contract DA-36-034-ORD-1216RD. With this acknowledgment to the Office of Ordnance Research, it is appropriate to include in the present report a description of the experiments which were performed during the period of joint sponsorship of the program by ONR and OOR. Shortly after the termination of Contract Nonr 198(00) on Jan. 31, 1954 the Office of Ordnance Research, cognizant of the intimate relationship between the theoretical and experimental aspects of this problem, enlarged the scope of its contract to provide for the continuation of the theoretical investigations in the light of the nature of the results which had been obtained thus far.

This report will be divided into two sections, of which Section I will discuss purely theoretical matters, whereas Section II will deal primarily with the experimental results, including their theoretical interpretations.

## II. THEORETICAL

### (A) General Remarks.

Initial emphasis was given to a detailed examination of the existing knowledge regarding secondary electron emission, and the most significant conclusions were discussed in a published paper, a reprint of which is attached herewith.

A critical evaluation of existing theories was undertaken in order to arrive at a decision as to which of the following alternatives would provide the greatest promise for fruitful results:

- 1) An extension of existing theories.

This would be accomplished by affecting various improvements of the underlying assumptions, and adding refinements such as a more detailed treatment of the basic processes involved;

- 2) A search for a new model of secondary electron emission independent of any previous theories.

Several alternative models might be pursued simultaneously.

Critical consideration led to the conclusion that alternative (2) was most advantageous, particularly in view of the rather fundamental limitations inherent in existing theories, and their basic inability to predict physical consequences except in very limited instances. The remainder of this section will be devoted to a summary of some of the more significant results of this line of attack.

### (B) Analysis of Secondary Electron Emission by the Method of Virtual Quanta.

In the study of the interaction of high energy electrons with matter (e.g. excitation of nuclei, or ionization of atoms)



satisfactory results can be obtained in many cases by treating the field of the electron as if it were composed of gamma-ray quanta traveling with the electron. The number of such quanta to be associated with the electron is determined by a Fourier analysis of the electronic field. If one knows, either experimentally or theoretically, the probability that a given process will occur when a material is bombarded by gamma-rays, it is then possible to determine the probability that electronic bombardment will excite the same process. The electron problem, which in many cases would be a very difficult one, is thus reduced to a problem which has already been solved, and to a Fourier analysis which is the same for all types of interaction.

The method outlined above is valid, in general, only if the energy of the bombarding electrons is high, i.e. if their velocity is nearly that of light. However, under certain limiting conditions, the method is useable for low velocity electrons as well. Consequently, it was considered worth while to attempt to adapt this procedure to the analysis of the phenomenon of secondary electron emission, even though it was not known whether these conditions were actually satisfied.

Application of this technique to the problem of secondary emission led to results which were in remarkably good agreement with experiment. It was possible to make rough estimates of the absolute value of the number of secondaries per incident primary to be expected from metals (yield  $\delta \approx 1$ ) for all elements investigated, and an exact expression for the energy dependence of the yield was derived. Baroody has pointed out (E. M. Baroody, Phys. Rev. 78, 780 (1950)) that if  $\delta/\delta_{\max}$  (secondary yield/maximum secondary

yield) is plotted as a function of  $E_0/E_{\max}$  (primary energy/energy for maximum yield) a curve which is independent of the nature of the emitting metal is obtained. The method of virtual quanta predicts a universal energy-dependence of this type, and, furthermore, the calculated curve agrees with the experimental data within the experimental uncertainties.

Detailed investigation of the conditions for validity of the method revealed, however, that although valid in a certain approximation, it is, nevertheless, quite incorrect to employ it here in its exact form. Hence the excellent agreement with experiment must be regarded as fortuitous. Furthermore, in its correct form, the method of virtual quanta is exactly equivalent to the Born approximation which can be utilized directly just as easily. Consequently, further application of the method was abandoned.

### (C) The Origin of Secondary Electrons

A fundamental question in the theory of secondary emission is whether most of the secondaries come from the conduction band or from more tightly-bound levels. This problem was investigated in detail for the case of copper, and it appears that the conclusions thus obtained should apply at least qualitatively to other metals.

The number of internal secondaries, produced per unit path of the primary, with sufficient energy to overcome the surface barrier is computed on the basis of the following assumptions: (a) the conduction electrons can be treated as free; (b) the wave functions for the bound electrons are the same as those for the corresponding states in isolated atoms.

The calculations revealed that, in the case of copper,

only the M electrons and the conduction electrons are important sources of secondaries, and that roughly twice as many secondaries come from the M shell as from the conduction band.

Consequently, we can expect that the bulk of the secondaries originate in the bound states in most metals. Hence, in developing a theory of secondary electron emission, it is essential to take this fact into account.

(D) The Interaction of the Primary with the Conduction Electrons.

The results of an investigation of the interaction between the primary and conduction electrons have been discussed in a note published in The Physical Review, a reprint of which is attached herewith. The principal conclusions are that the Wooldridge theory of secondary emission is incorrect, and that the correct expression for the rate of production of internal secondaries is very similar in form to that obtained by Bethe for the ionization of gases.

(E) The External Secondary Yield.

Utilizing the results of the previous sections concerning the production of internal secondary electrons, an expression for the energy-dependence of high energy secondary emission can be derived. On the basis of certain assumptions regarding the escape probability, it is then possible to discuss the influence of primary scattering on low energy secondary emission.

From the theory of the primary interaction, the rates of production of secondaries and of primary energy loss are given by

$$U(E) = \frac{A}{E} \ln \frac{E}{\epsilon} \quad (1)$$

and

$$\frac{dE}{dx} = - \frac{B}{E} \ln \frac{E}{\eta} \quad (2)$$

where  $U(E)$  represents the number of secondaries produced per unit path by a primary of energy  $E$ ,  $\frac{dE}{dx}$  is the rate of energy loss, and  $A, B, C, \eta$  are constants independent of the primary energy. These expressions are valid regardless of whether the secondaries are assumed to originate only in the conduction band or in deeper-lying levels as well.

In order to obtain the external secondary yield, Eq.(1) is multiplied by the probability of escape of the secondaries, and integrated over the range of the primary. If we assume that the secondaries escape by some sort of diffusion process, the probability of escape of a secondary,  $p(x)$ , depends only upon  $x$ , the depth below the surface at which it is produced. The secondary yield is then given by:

$$\delta = \int_0^R p(x) U(E) dx \quad (3)$$

where  $x$  is the distance traversed by the primary, measured along its path, and  $R$  its range.

For primaries of sufficiently high energies,  $U(E)$  is practically constant over that portion of the primary path from which the secondaries can emerge. Furthermore, the primaries are not scattered appreciably. Consequently  $E$  is approximately equal to the incident energy  $E_0$ , and  $x \approx z$  over the region in which  $p(x)$  is appreciably different from zero. We then obtain:

$$\delta = U(E_0) \int_0^\infty p(x) dx \quad (4)$$

which reduces to

$$\delta = \frac{C}{E_0} \ln \frac{E_0}{\epsilon} \quad (5)$$

since  $p(x)$  is independent of the primary energy. Thus, independently of the basic assumptions, any theory of secondary emission should reduce to the  $E_0^{-1} \ln E_0$  form at high energies.

At low energies the situation is more complicated, inasmuch as  $E$  can no longer be treated as constant. Consequently,  $U(E)$  cannot be taken outside the integral and the expression for  $\delta$  will involve the explicit form of the escape probability function. For ease of computation, we shall assume that this function can be approximated by a simple step, i.e. no secondaries produced beyond a certain distance,  $L$ , from the surface can escape, whereas a constant fraction (independent of primary energy) of the secondaries created within the critical distance emerge. This would correspond roughly to a range-energy relationship for the secondaries.

Under these conditions, we have

$$p(x) = \alpha, \quad x < L \quad (6)$$

$$p(x) = 0, \quad x > L$$

and if it is further assumed that the primaries are unscattered, the expression for  $\delta$  becomes:

$$\begin{aligned} \delta &= \alpha \int_0^L U(E) dx \\ &= -\alpha \int_{E_L}^{E_0} \frac{U(E)}{\frac{dE}{dx}} dE. \end{aligned} \quad (7)$$

If all of the primary energy is expended in the production of secondaries,  $\frac{dE}{dx}$  is proportional to  $U(E)$  and Eq. (7) becomes

$$\delta = D[E_0 - E_L] \quad (8)$$

where  $E_0$  is the incident energy of the primary,  $E_L$  its energy after penetrating to depth  $L$ , and  $D$  a constant independent of energy. Actually, the last assumption is unnecessary and (8) is a very good approximation to (7) even if the primary loses energy by processes other than the production of secondaries.

The quantity  $(E_0 - E_L)$  may be obtained as a function of  $E_0$  by the integration of Eq. (2). The resultant yield vs. energy curve is found to be very insensitive to the choice of parameters, and is thus nearly independent of target material.

The results of the calculation are shown in Fig. 2, where  $E_0$  is the primary energy, and  $E_{\max}$  the energy at which the maximum yield,  $\delta_{\max}$  is obtained. Curve A is a normalized empirical plot of yield vs. energy for metals, which as was at first pointed out by Baroody, is nearly independent of material. Curve B is a typical plot of  $(E_0 - E_L)$  normalized to unity at the maximum. While the two curves are very nearly parallel at higher energies, corresponding to the  $E_0^{-1} \ln E_0$  form, curve B falls off much too rapidly at low energies. This rapid decrease is attributable to the fact that the effect of primary scattering has been neglected.

That taking into account the effect of primary scattering is in the direction of removing this discrepancy is readily demonstrated. In the model which has just been discussed, the following situation prevails:

A primary of energy  $E_0$  strikes the surface and continues undeflected until it reaches the end of its range. If its range is less than  $L$ , all of its energy will be expended in the region from which secondaries can escape, and the yield is simply proportional

Fig. 2

Universal curve of secondary electron emission as a function of the energy of the primaries. The ratio of the yield,  $\delta$ , to the maximum value of the yield,  $\delta_{\max}$ , for a particular target is plotted as ordinate, and the corresponding ratio  $E_0/E_{\max}$  as abscissa. Curve A fits most of the available experimental data. B is the theoretical curve derived on the basis of the assumptions discussed in the text, neglecting the effect of scattering of the primaries. When this is taken into account, curve C is obtained. The discrepancy between curves C and A can be reduced by assigning a larger value to the arbitrarily-estimated scattering parameter assumed in the computation. The influence of primary scattering displays the predicted qualitative effect, i.e. it flattens the yield vs energy curve.

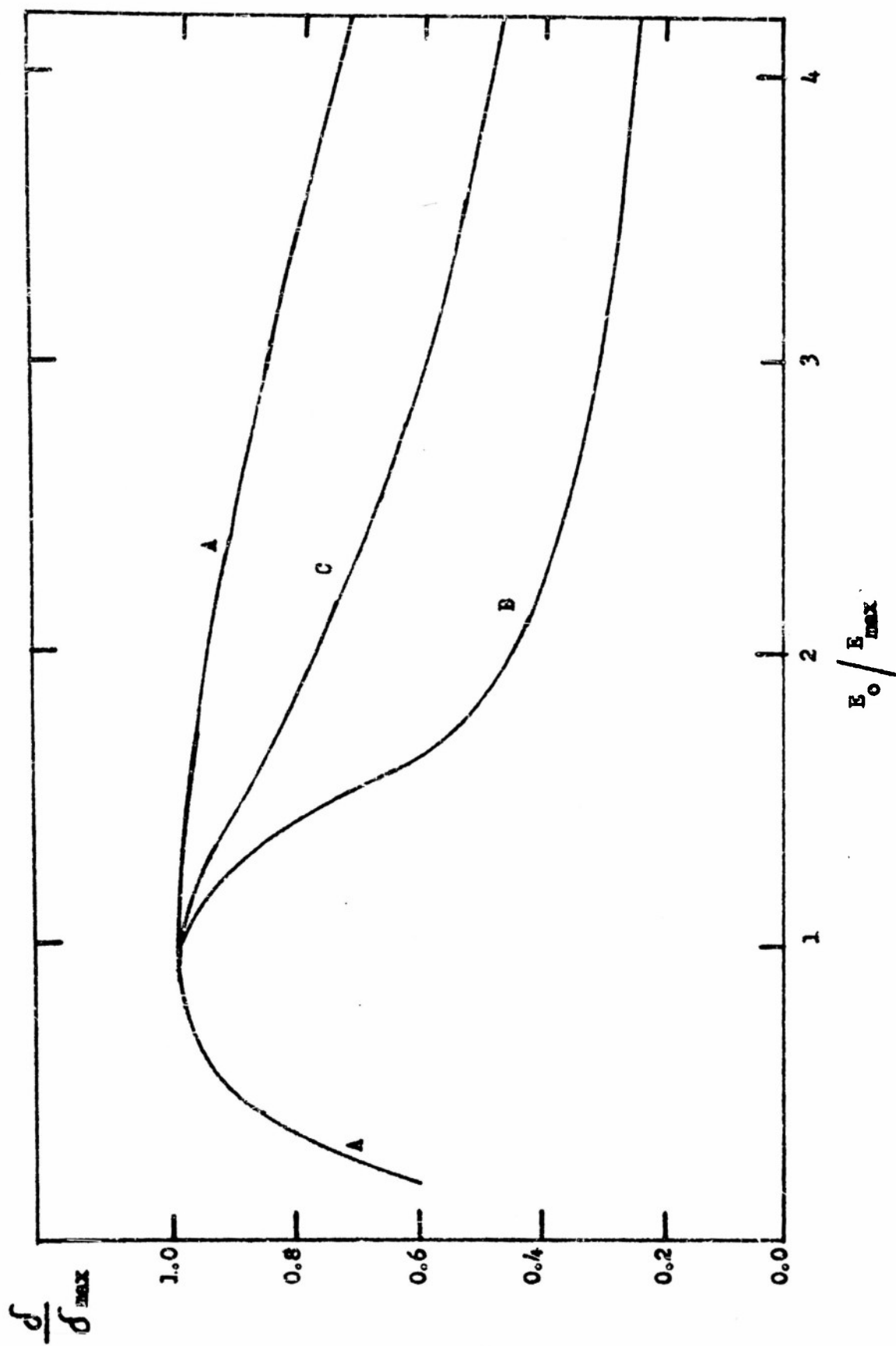


Fig. 2



to the primary energy. After the range has exceeded  $L$ , the yield will decrease fairly rapidly as the energy increases, and the condition in which most of the secondaries are produced beyond the escape depth will be attained quickly. For example, at a primary energy  $E_0 = 2 E_{\text{max}}$  about 75 percent of the secondaries are produced at distances from the surface greater than  $L$ . If primary scattering is taken into account, however, this situation is modified considerably. Many primaries having energies near the maximum of the yield vs. energy curve are so strongly scattered that their paths lie entirely within the escape region. The number of secondaries produced by these scattered primaries increases linearly with energy, and partially compensates for those which would otherwise have been produced too far from the surface to emerge. This effect tends to flatten the yield vs. energy curve.

To investigate the problem somewhat more quantitatively, we make the following assumptions with respect to the escape process:

(1) The primaries are either stopped within depth  $L$  or pass through it undeflected. Of course, this is not an accurate description, but it should represent the average behavior to a sufficient approximation for the present purposes.

(2) The fraction of primaries stopped in the "escape region" is proportional to  $L/R$ . Examination of  $\beta$ -ray absorption curves reveals that, at least for high energy electrons, the proportionality constant ( $\tau$ ) should be somewhat greater than one.

Eq. (8) modified to take into account the influence of primary scattering, then becomes

$$\delta = D(1 - \tau \frac{L}{R})(E_0 - E_L) + D \tau \frac{L}{R} E_0 \quad (9)$$

The first term represents the contribution to the yield of secondaries produced by primaries that pass beyond the escape region, and the second the contribution by those that are stopped therein. The results of the computation with  $\bar{\nu} = 1$  are shown in Fig. 2, Curve C. The influence of scattering displays the predicted qualitative effect. The discrepancy between the theoretical curve C and empirical curve A can be ascribed, at least in part, to the fact that the effect of scattering probably exceeds that corresponding to the assignment of the value unity to  $\bar{\nu}$ .

It is of interest to note the importance of the role played by primary scattering in the phenomenon of secondary emission. At  $E_0/E_{\max} = 2$ , almost all of the emergent secondaries are produced by the strongly-scattered primaries, even though only about  $1/3$  of the primaries are in that category. At  $E_0/E_{\max} = 4$ , scattered and unscattered primaries contribute about equally. At higher bombarding energies, scattering becomes unimportant, and the expression for  $\delta$  reduces to the form given by Eq. (5).

Although the approximations made in this analysis are admittedly rather crude, the agreement between theory and experiment is fairly good. Furthermore, the model based upon a simple step function for the escape probability is probably more realistic than the commonly-used exponential absorption law, and the qualitative conclusion that primary scattering plays a dominant role in low energy secondary emission is undoubtedly correct.

### III. EXPERIMENTAL

#### (A) General Remarks.

The experimental program has been directed toward the study of secondary emission under conditions such that the primaries pass through the target without appreciable energy loss, so that we are dealing with secondaries produced by monoenergetic primaries in contrast to the usual situation in which thick targets are bombarded by low energy primaries. In the latter case, the secondaries are produced by primaries of all energies up to their initial energy.

In all of the measurements which have been obtained thus far, the target has been exposed to the primary beam which passes through it essentially undisturbed, producing secondaries which can emerge from either the front or back face. The yield is then determined by measuring the ratio of the secondary currents to the primary current. Targets of various elements ranging over the periodic system from carbon to gold, as thin as  $5 \times 10^{-6}$  inches and as thick as  $10^{-2}$  inches, have been bombarded and the following quantities have been measured:

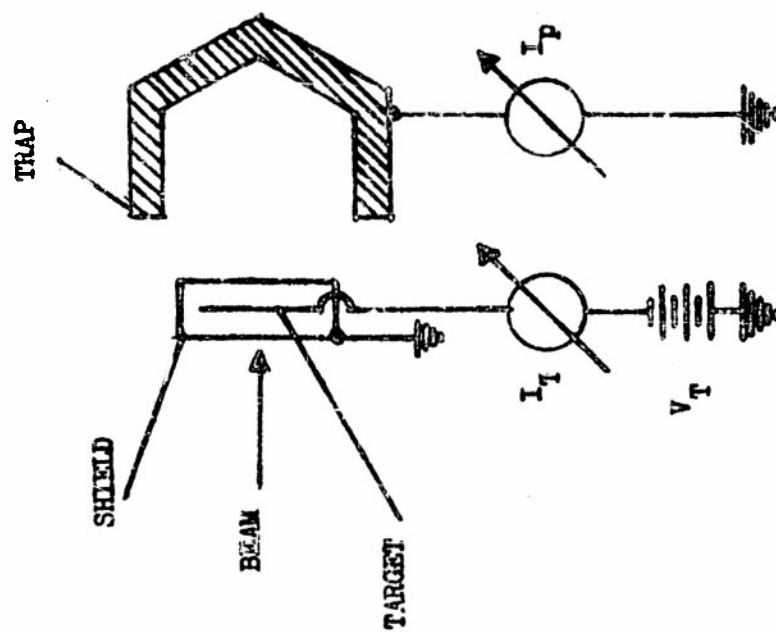
- 1) The combined yield of low energy secondaries from both faces of the target;
- 2) The ratio of the low energy yield from the exit face of the target to that from the entrance face;
- 3) The yield of high energy secondary electrons ( $E > 2$  kev).

#### (B) Low Energy Secondaries.

The general method of measurement is shown in Fig. 3. The beam passes through a carbon collimator, then through a sandwich arrangement, consisting of the target surrounded by a thin

Fig. 3

Schematic diagram of sandwich arrangement for measuring secondary electron emission from thin targets through which the primary beam passes essentially undisturbed. The beam enters through a carbon collimator, then passes through the electrodes consisting of the target surrounded by a thin foil shield, and is finally stopped by the carbon trap. The method of determining the yield from the measurements in terms of the accompanying equations is explained in the text.



- (1)  $V_T > 0 : I_T = I - S$
- (2)  $V_T < 0 : I_T = I - S > V_T$
- (3)  $V_T = 0 : I_T^0 = I - S$

Fig. 2

Fig. 4

Typical energy distribution obtained by the method illustrated in Fig. 3. The yield of secondaries per impinging primary,  $I_s(E_X)/I_p$ , having  $X$ -associated energy less than that corresponding to  $V_T$  is plotted as a function of the retarding potential.

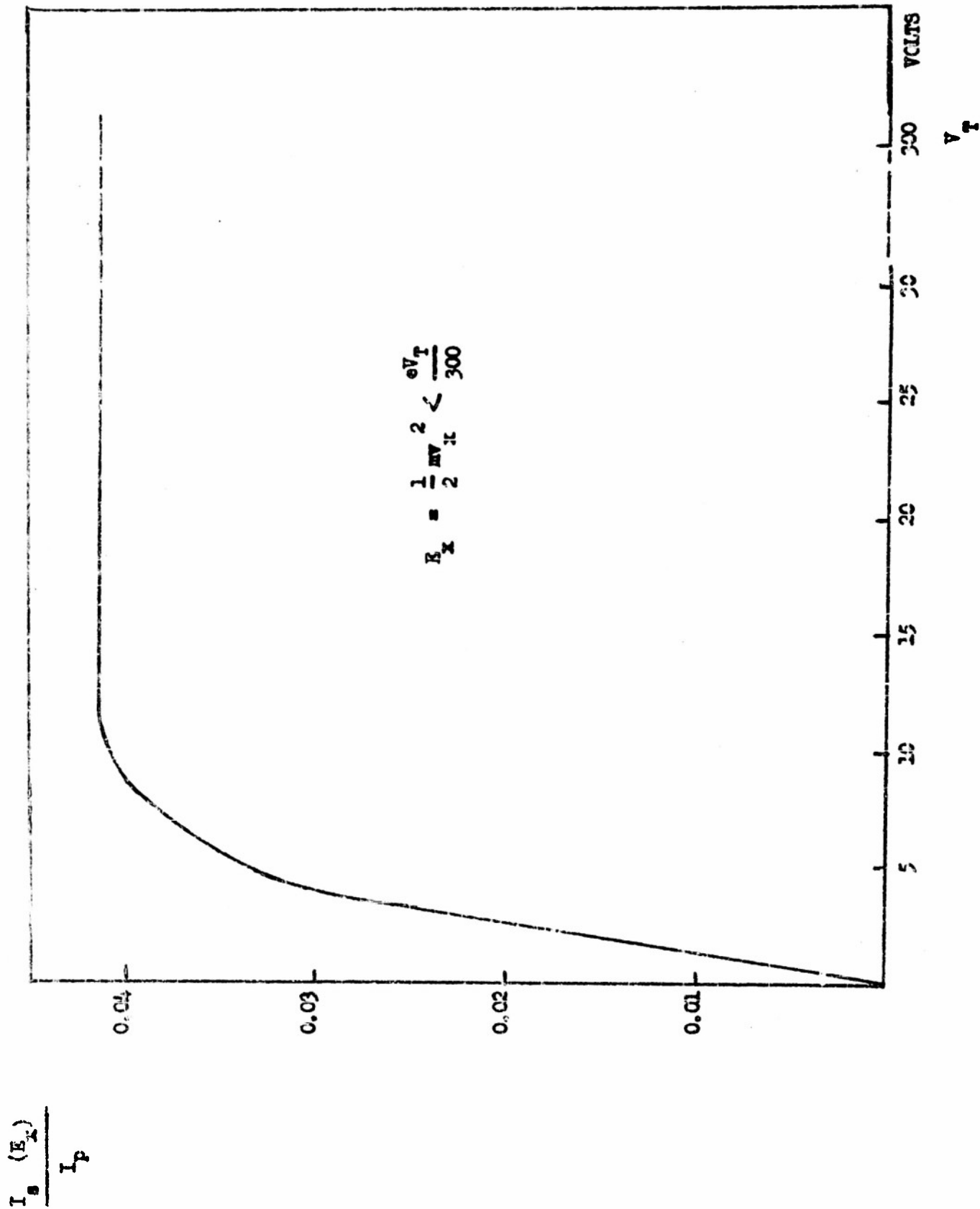


Fig. 4

foil shield, and is finally stopped by the carbon trap. The sandwich arrangement is necessitated by the fact that the target must be shielded from stray secondaries produced in the collimator and trap. The yields are calculated from the equations shown on the right. In Eq. (1)  $I_T^+$  represents the measured current of electrons from the target when the target is biased positively with respect to the shield by  $V_T$  volts. Under these conditions only those electrons can leave the target whose normal velocity component is sufficient to overcome the retarding potential  $V_T$ , while all the secondaries produced on the inside faces of the shield reach the target. The net target current is then the difference between the current of target secondaries,  $T > V_T$ , and the current of secondaries reaching the target from the shield,  $S$ . Eq. (3) represents the condition when the target and shield are at the same potential. The net target current,  $I_T^0$ , is then the difference between all of the secondaries emitted by the target and those emitted by the shield. Subtracting (3) from (1) and dividing by the primary current, one obtains the yield of secondaries with X-associated energy less than  $V_T$ . A typical integral energy distribution obtained by this method is shown in Fig. 4. Here, the yield of secondaries (measured as a fraction of the primary current  $I_p$ ) with X-associated energy  $< V_T$  is plotted as a function of the retarding potential,  $V_T$ . (This is the inverse of the usual distribution in which is plotted the yield of electrons of energy  $> V_T$  vs.  $V_T$ ). The form of the distribution is typical of those obtained with all targets (this one being 0.0005 in. Ni) and in the low energy region is very similar to that observed with low energy primaries. The maximum of the corresponding differential distribution occurs at about six volts, and there is no observable intensity of secondaries in the energy range from



20 ev to 2000 ev. The saturation value of the emission with high  $V_p$ , which is the yield of low energy secondaries, is about 4 percent, and varies from about 2 percent to 4 percent for the other targets we have measured. These values in themselves are not too significant, since the measurements were made in the vacuum system of the linear accelerator and the surfaces were consequently not free of contaminations. A sealed-off tube (Fig. 5) has been constructed for measuring the yields of targets degassed under good vacuum conditions, the beam being admitted through a thin glass window, and it is anticipated that the yields will be somewhat lower than those cited above.

(C) Forward-Backward Ratio.

The experimental arrangement for the measurement of the relative yields from the entrance and exit faces of the target is shown in Fig. 6. It differs from the arrangement already discussed only in that the potentials of the shields opposite the two faces of the target can be varied independently. By fixing the potential of one shield, and varying the other, the yield from the corresponding face of the target can be obtained. For example, by holding  $V_2$  constant and varying  $V_1$  the low energy secondary yield from the entrance face can be measured, and by reversing the process the yield from the exit face can be determined. This measurement has been performed with a .0001 in. Ni target, with the result that the yields from the two faces were found to be essentially the same. The observed ratio is:

$$\frac{\delta_2}{\delta_1} = 1.02 \pm 0.05.$$

In order to insure that this result was not a consequence of different surface conditions of the two target faces, the experi-

Fig. 5

Sealed-off tube for measuring secondary electron emission from clean metal surfaces by the sandwich method. The beam is admitted through a thin glass window, after which it passes through a carbon collimator into the system of electrodes shown schematically in Fig. 6. By means of a magnetic plunger, the target and shields may be removed from the beam to determine the effect of stopped primaries which may become appreciable with thicker targets. The sandwich is heated by bombardment with electrons from two adjacent groups of filaments between which the assembly rests during processing on the exhaust system.



Fig. 6

Experimental arrangement for the measurement of the relative yields from the entrance and exit faces of a thin target.

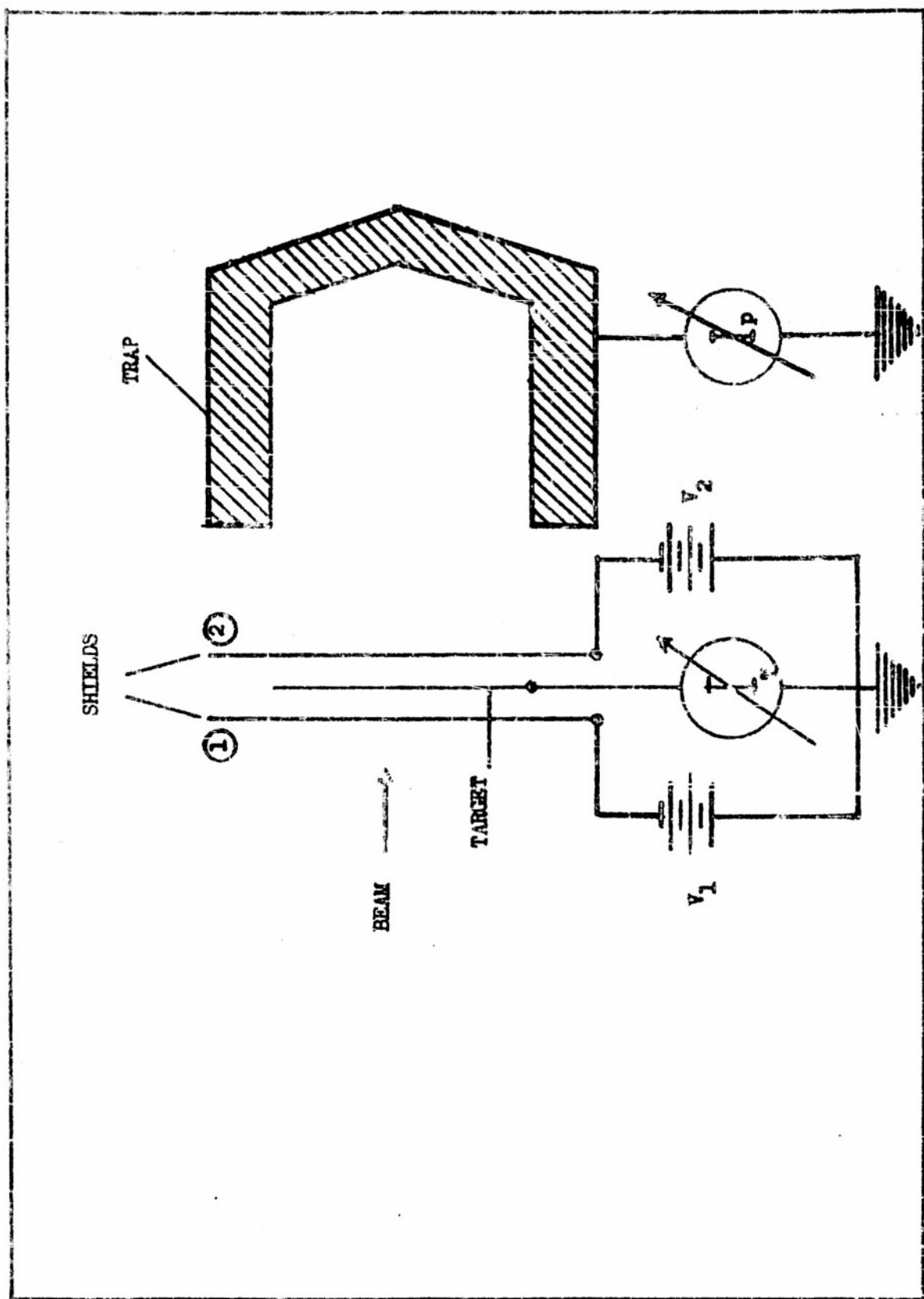


Fig. 6

ment was repeated after rotating the target through  $180^\circ$  in vacuum, thus interchanging the front and back faces of the foil. The yields were found to remain unchanged.

This result indicates the importance of the scattering of the secondary electrons while traversing the path from their point of origin in the target to the surface. Were it not for this factor, a preponderance of secondaries would be expected to emerge in the direction of travel of the beam, in view of the conservation laws which must apply in the interaction between the primary and the atomic electrons.

(D) High Energy Secondaries.

In the course of the investigations of low energy secondaries, it was found that a relatively large group of high energy secondaries (with energies  $> 2000$  ev) is also emitted, and these have been studied in some detail. This subject is discussed in the following manuscript, which has been submitted for publication. This paper also contains a description of the demountable experimental tube with which the measurements have been obtained, as well as general information regarding the linear accelerator.

EMISSION OF ENERGETIC SECONDARY ELECTRONS PRODUCED BY 1.3 Mev  
ELECTRON BOMBARDMENT\*

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Bartol Research Foundation of The Franklin Institute, Swarthmore, Pa.

Abstract

The emission of energetic secondary electrons (delta rays or knock-on electrons) produced by 1.3 Mev primaries which penetrate thin targets with negligible mean energy loss has been investigated. These have previously not been observable in the customary thick-target experiments because of the inherent impossibility of distinguishing between true secondaries and reflected primaries which have suffered large energy losses. The present arrangement does not record back-scattered primaries, but only emitted electrons. The delta ray yields from various targets (Al, Ni, Au, Ag, Cu, C) ranging in thickness from  $5 \times 10^{-6}$  to  $10^{-2}$  in. have been measured. The determinations of  $I_s / I_p$  vary between 0.3 percent and 2.1 percent independent of surface treatment, and there is only a small dependence of the yield upon target material for an equivalent thickness expressed in  $\text{mg cm}^{-2}$ . For  $45.8 \text{ mg cm}^{-2}$  Ni, the delta ray yield is  $2.08 \pm 0.15$  percent. This may be compared with  $1.48 \pm 0.25$  percent, the yield of low-energy secondaries as measured with the cleanest surface attainable in the demountable experimental tube.

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## I. Introduction

Although secondary emission from solids bombarded by electrons having energies below several thousand ev has been the subject of considerable investigation, the advantages of extending the observations to high primary energies have remained generally unrecognized. Sources of electrons in the Mev region have been available for many years, and numerous studies of electron scattering have been conducted. Nevertheless, the only previous secondary emission measurements have been those in the range from 30 kev to 340 kev obtained by Trump and Van de Graaff<sup>1)</sup> with the electrostatic generator in the course of experiments directed primarily at investigating the mechanisms of voltage breakdown in high vacuum, and from 18 kev to 1.4 Mev by Miller and Porter<sup>2)</sup> with the linear accelerator.

The conventional arrangement for measuring the yield of secondary electrons involves a thick target in which the primary is completely absorbed. When the bombarding energy is low, the description of the phenomenon of secondary emission comprises essentially four processes, some of which are not particularly amenable to theoretical analysis. These are: (1) the primary interaction, (2) the primary energy loss, (3) the escape of secondaries, and (4) integration of the first three steps over the range of the primary. By invoking a combination of very high primary energy and targets which are sufficiently thin to permit the bombarding electrons to pass through with negligible scattering and energy loss, a significant simplification of the theoretical treatment results. For this reason, and in order to study certain other aspects of secondary electron emission, a program of experiments was undertaken



utilizing the multiple-cavity linear accelerator as the source of a 1.3 Mev electron beam. In contrast with the methods employed previously, the present techniques have permitted the direct observation of energetic secondary electrons, long familiar to cosmic ray investigators as knock-on electrons or delta rays.

## II. Experimental Procedure

### A. Method

The electrons leaving a bombarded target can be ascribed to three different mechanisms. Some of the primary electrons are directly reflected, whereas others are scattered with some loss of energy. Finally, secondary electrons are emitted by the target as a consequence of interactions between the primary electrons and the electrons in the solid. In the usual experimental arrangement, which is illustrated schematically in Fig. 1, it is impossible to distinguish between true secondaries and reflected primaries which have suffered large energy losses. In this case, the target current,  $I_P - I_S - I_{RP}$ , is the difference between the total primary current and the current of secondary electrons plus back-scattered primaries which do not return to the target. The collector current is composed of both secondary electrons leaving the target,  $I_S$ , and primaries scattered from the target,  $I_{RP}$ . The classification in terms of secondaries and scattered or reflected primaries is made on the basis of the energy distribution of the collected electrons, obtained by applying retarding potentials,  $-V_C$  to the collector with respect to the target. Collected electrons which can overcome some rather arbitrarily-assigned retarding potential are then regarded as scattered and reflected primaries, whereas the electrons of lower energies are designated

Fig. 1

Conventional arrangement for measuring secondary electron emission from thick targets. It is impossible to distinguish between energetic secondaries and back-scattered primaries in this case.

Fig. 2

Arrangement for measuring secondary electron emission from thin targets through which the primaries pass with negligible energy loss. Primaries scattered from the target are not recorded.

Fig. 1

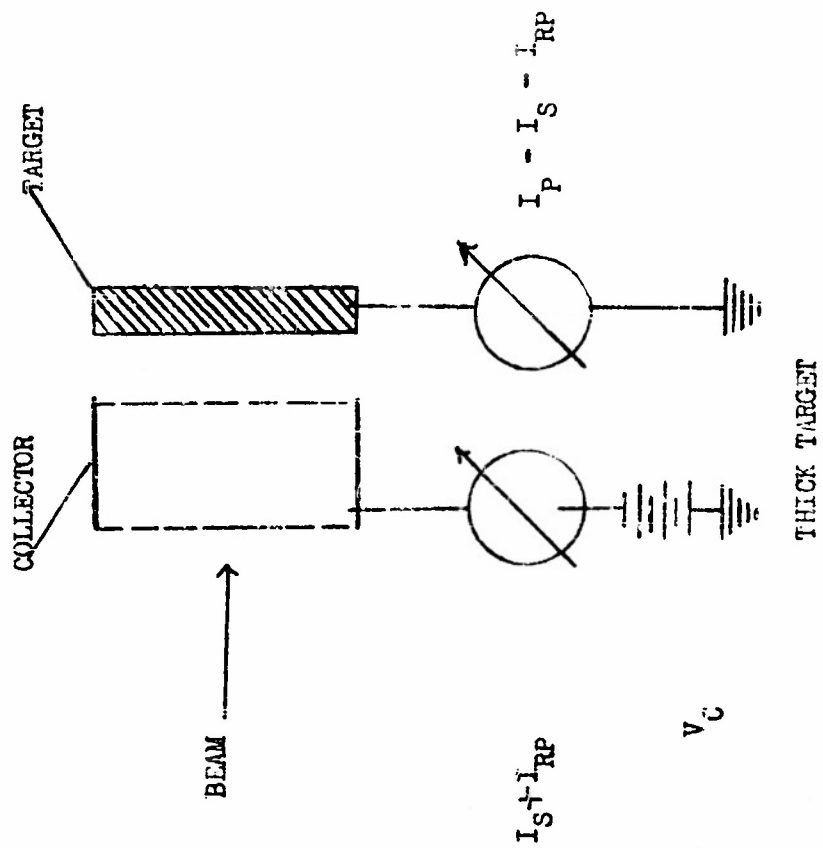
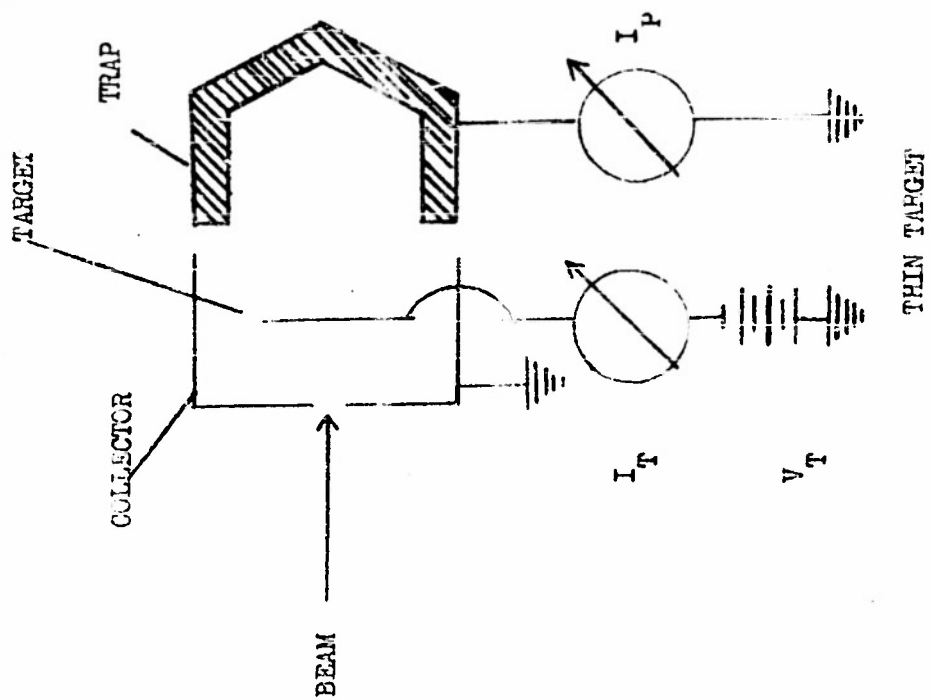


Fig. 2



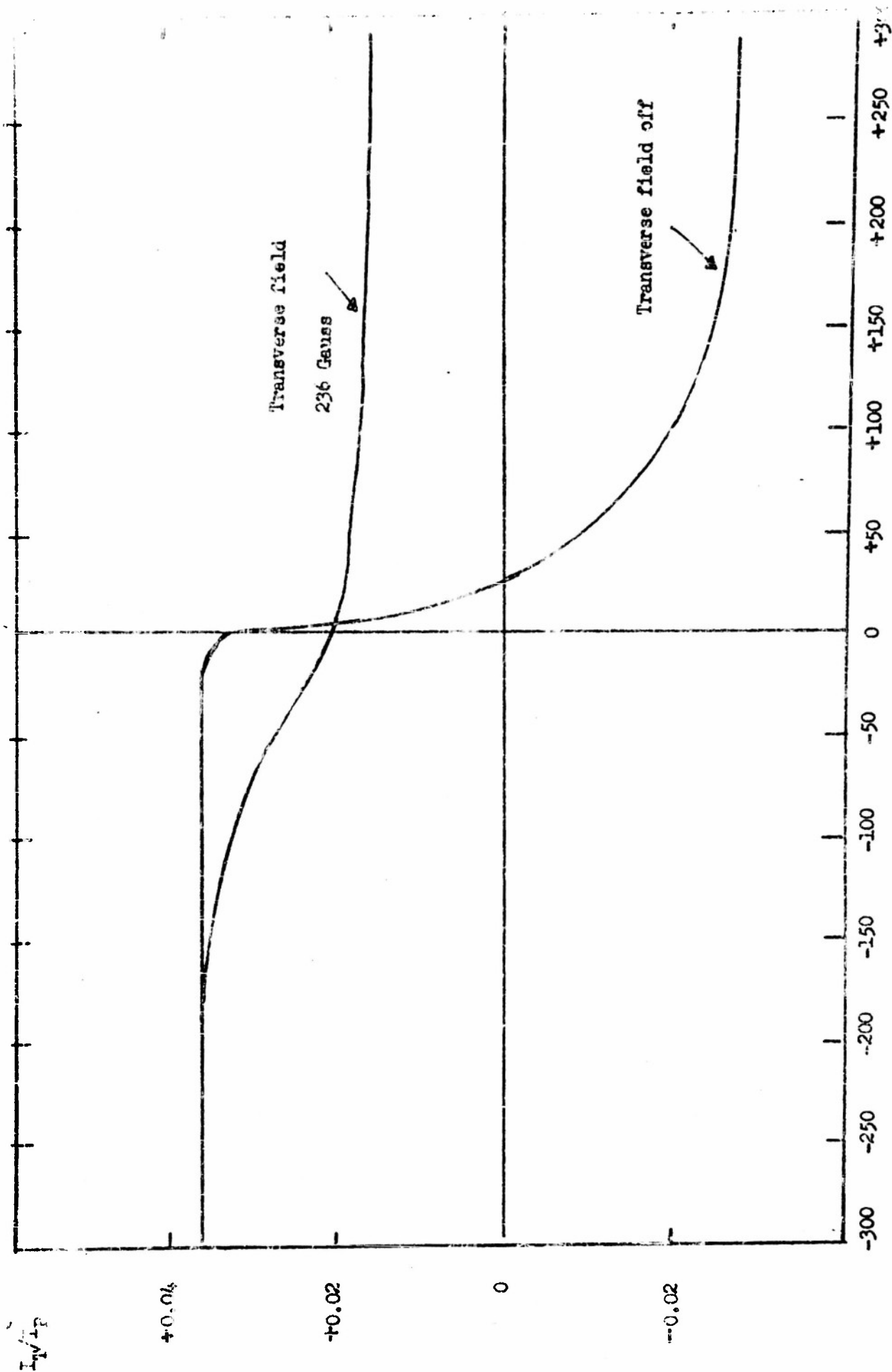
as true secondaries. Thus, high energy secondaries and scattered primaries are indistinguishable, and the contribution of the former to the total yield is, in fact, assumed to be negligible.

In the present arrangement, shown in Fig. 2, the scattered primaries are not recorded. When the potential of the target is positive with respect to the surroundings, the target current,  $I_T$ , represents the difference between those secondaries which have sufficient energy to overcome the retarding potential,  $V_T$ , and the secondaries from the surroundings (trap and collector electrodes) which are attracted to the target. The primary beam penetrates the target, and is observed as the trap current,  $I_p$ , the magnitude of which is unaffected by the presence of the target. The secondaries from the surroundings can be prevented from reaching the target by the application of a transverse magnetic field of appropriate magnitude in the vicinity of the target, thereby permitting the determination of the delta ray yield.

The effect is revealed in Fig. 3, which shows the dependence of the ratio <sup>3)</sup>  $I_T/I_p$ , upon target potential,  $V_T$ , with a transverse magnetic field either on or off. With no magnetic field, all of the secondaries leave the target when  $V_T$  is negative. In this case, low energy secondaries from the surroundings are repelled by the target, although high energy secondaries may be collected. However, when the target potential is between -15 v and zero, all extraneous low-energy secondaries are not retarded, and those which strike the target cause the net target current to decrease. When  $V_T$  is sufficiently positive, a net collection of electrons by the target occurs, since the low energy secondaries from the surroundings are now

Fig. 3

Dependence of  $I_T/I_P$  upon  $V_T$  (cf. Fig. 2) with and without a transverse magnetic field. The ratio is defined as positive when there is a net emission of electrons from the target.



TARGET POTENTIAL,  $V_T$

Fig. 3

attracted, and the yield becomes negative. However, the application of a transverse magnetic field prevents the stray electrons from reaching the target, and a net emission is manifested by the positive yield.

This provides a lower limit for the delta ray yield, since both imperfect protection of the target from extraneous electrons and the return of emitted delta rays to the target tend to reduce the net target current. In practice, the measured value probably coincides with the actual value within the experimental uncertainty.

#### B. Tube Design

The arrangement of the electrodes in the demountable experimental tube is shown in Fig. 4. The tube is attached to a magnetic spectrum analyzer by means of a flange with an O-ring gasket at the output end of the linear accelerator.

The graphite collimator defines the size of the primary beam, which is approximately 6 mm in diameter at the target. The eccentric pumping holes provide adequate pumping speed without the introduction into the target region of the copious background of stray electrons from the analyzer.

The target is supported by a rod equipped with a sliding O-ring gasket arrangement (not illustrated) which permits positioning the 1" x 1 1/4" foil in or out of the path of the beam by remote control. The graphite trap which collects the primary electrons after they have penetrated the target can also be moved in vacuum to facilitate observations of any possible dependence of the results upon geometrical factors. In order to preclude the influence of

Fig. 4

Cross-sectional view of experimental tube utilized  
for determination of secondary electron yields.



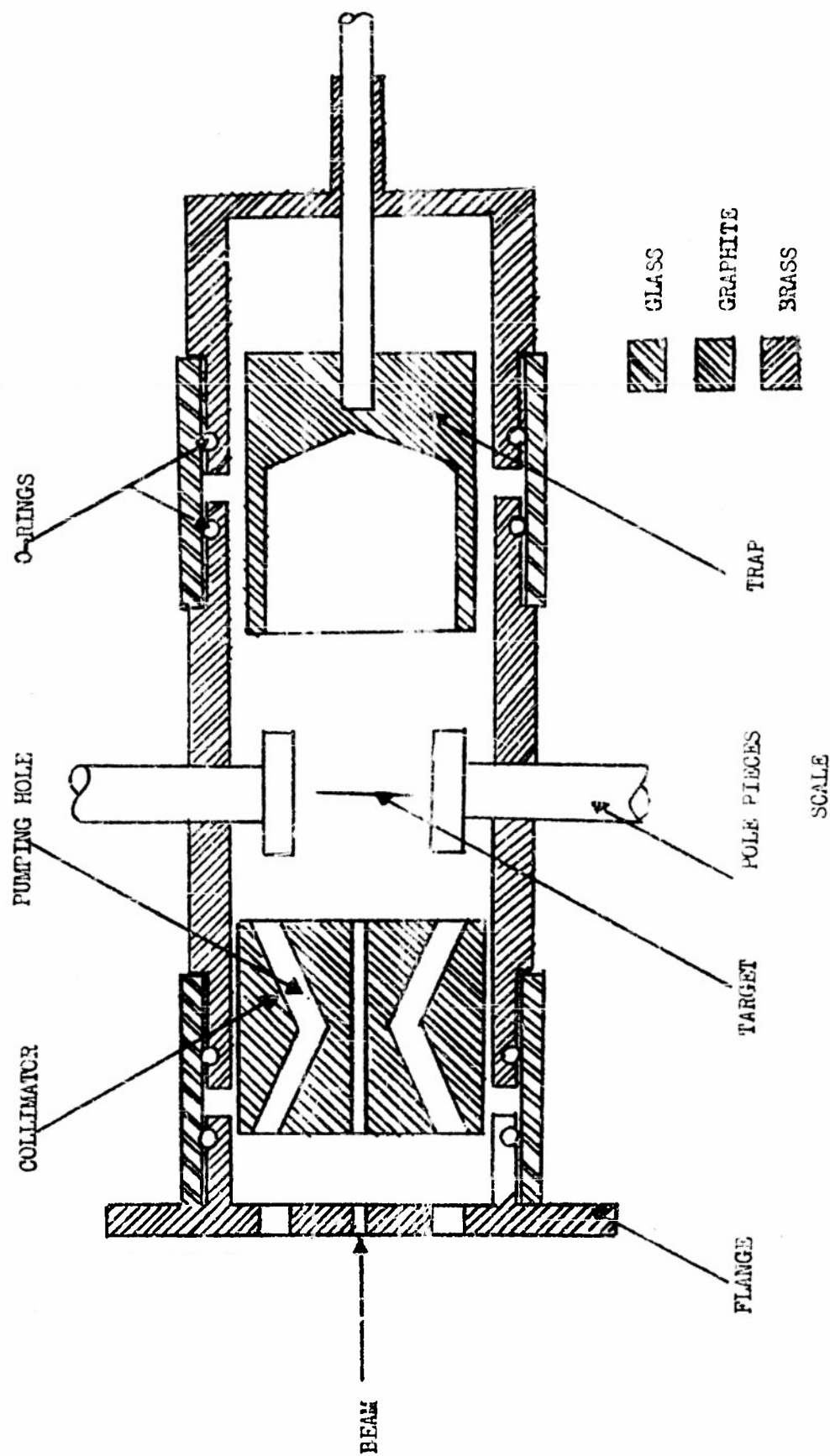


FIG. 4

ionization currents generated by the intense x-ray background, coaxial leads (not shown in Fig. 4) insulated from the brass envelope, are introduced through vacuum seals.

### C. Linear Accelerator and Auxiliary Apparatus

The essential features of the four-cavity linear accelerator<sup>4)</sup> utilized in these experiments have been described previously. Several modifications have produced a high degree of stability in operation, and the maximum attainable output current has been increased to peak values of 60 ma at 1.3 - 1.5 Mev by removal of the buncher cavity and improvements in the electron injection system. In the present measurements, the targets were generally bombarded by rectangular one microsecond pulses of primary electrons at a repetition rate of 20 pulses per second and pulse-height 0.05 - 1.0 ma. The energy spectrum, determined by the geometry of the analyzer, is triangular with a half-width of 7 percent, corresponding to 94 kev at 1.35 Mev.

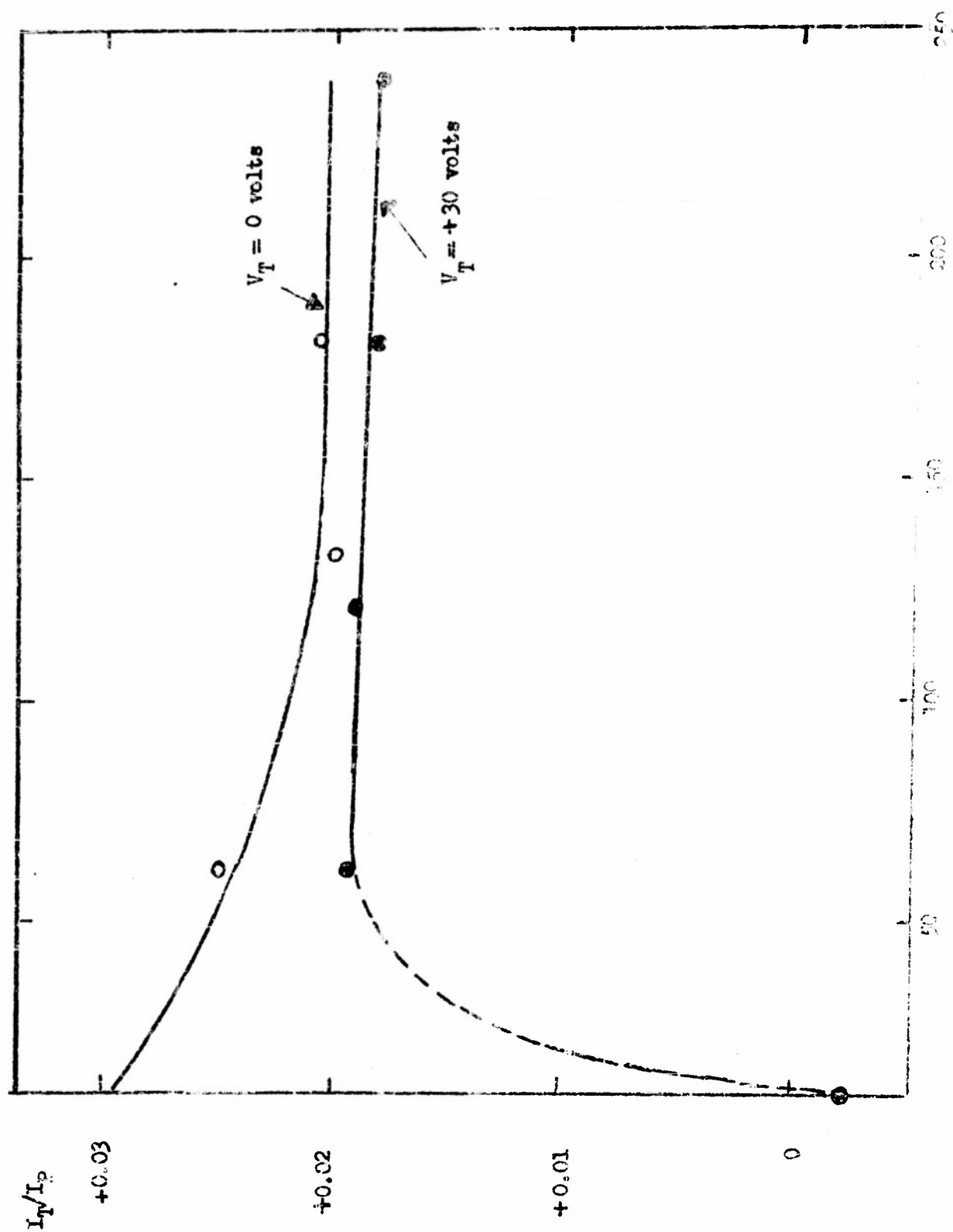
Trap and target currents are measured simultaneously by a pair of two-stage negative-feedback d.c. amplifiers<sup>5)</sup> with integrating networks in the input. The maximum sensitivity is  $10^{-12}$  amps per division, and the variation in the calibration of the electronic meters is less than 1 percent.

### D. Determination of Delta Ray Yields

Fig. 5 represents the series of observations comprising a typical delta ray yield determination. A potential as low as 18 v applied to the target with respect to its surroundings is sufficient to impede the escape of the low-energy secondaries produced in the target. However, in the absence of a transverse magnetic field, low-

Fig. 5

Typical series of observations of delta-ray yield.  
With  $V_T > 18$  v,  $I_T/I_p$  is measured as a function  
of the transverse magnetic field strength. Plateau  
values represent  $I_\delta / I_p$ .



TRANSVERSE FIELD - GAUSS

Fig. 5

energy secondaries emitted by the auxiliary electrodes are collected by the target, as a result of which a small net negative  $I_T/I_P$  is measured. When the transverse field is applied, stray low-energy secondaries are deflected away from the target, and with the field strength of appropriate magnitude, the target current is comprised primarily of electrons emitted by the target.  $I_T/I_P$  then remains constant over a "plateau" region of magnetic field strength. This reveals that a negligible contribution is attributable to extraneous effects. As confirmed by direct observation with a fluorescent screen placed at the position normally occupied by the trap, the primary beam is deflected considerably, and hence suffers appreciable scattering while traversing the collimator, when the field intensity exceeds a maximum value, which with the present arrangement is 240 gauss.

The delta ray yield of a particular target is determined from the average of at least eight individual measurements, with two different target voltages, spanning the magnetic field strength plateau. The dependence upon  $V_T$ , ( $V_T > +18$  v) is negligible.

#### E. Targets

Various metals (Al, Ni, Au, Ag, Cu) commercially available in coil, leaf, or sheet form, ranging in thickness from  $5 \times 10^{-6}$  in. (Au) to  $10^{-2}$  in. (Al) were employed as targets. Carbon targets were prepared by grinding the faces of a thin section sliced from a 1" diameter graphite rod.

In contrast with the conditions which prevail in measurements of low-energy secondary electrons, it is not necessary to exercise the customary precautions regarding surface cleanliness

in view of the high energy with which the delta rays emerge.

### III. Results

All of the determinations of delta ray yield are summarized in Fig. 6, where  $I_{\delta}/I_p$  is plotted as a function of target thickness expressed in  $\text{mg cm}^{-2}$ . The standard deviation of each point is approximately  $\pm 10$  percent of the indicated value. The experimental uncertainty is governed by fluctuations of the primary beam. Data obtained with a preliminary experimental tube having different dimensions from those indicated in Fig. 4 were in satisfactory accord with these results. Detailed comparison of total yields, including low-energy secondaries, was not attempted because of the dependence of the latter upon surface conditions. However, it is of interest to note the relative magnitudes of the yields of low and high energy secondaries from a typical target.

Although the delta ray yield was independent of surface treatment in all cases, the total yield invariably decreased when the target was degassed by electron bombardment from an adjacent filament in the experimental tube immediately prior to the measurement. The minimum low-energy yield from  $45.8 \text{ mg cm}^{-2}$  Ni subjected to the maximum practicable heating was  $1.48 \pm 0.25$  percent, a value which is presumably higher than that characteristic of an extremely clean specimen. The corresponding delta ray yield is  $2.08 \pm 0.15$  percent. Measurements of the yield of low-energy secondaries are now under way with sealed -off tubes processed in accordance with the procedures requisite for insuring the cleanliness of the target surfaces.

Fig. 6

Dependence of delta-ray yield from various materials upon target thickness. The solid curves represent the theoretical predictions discussed in Section IV.

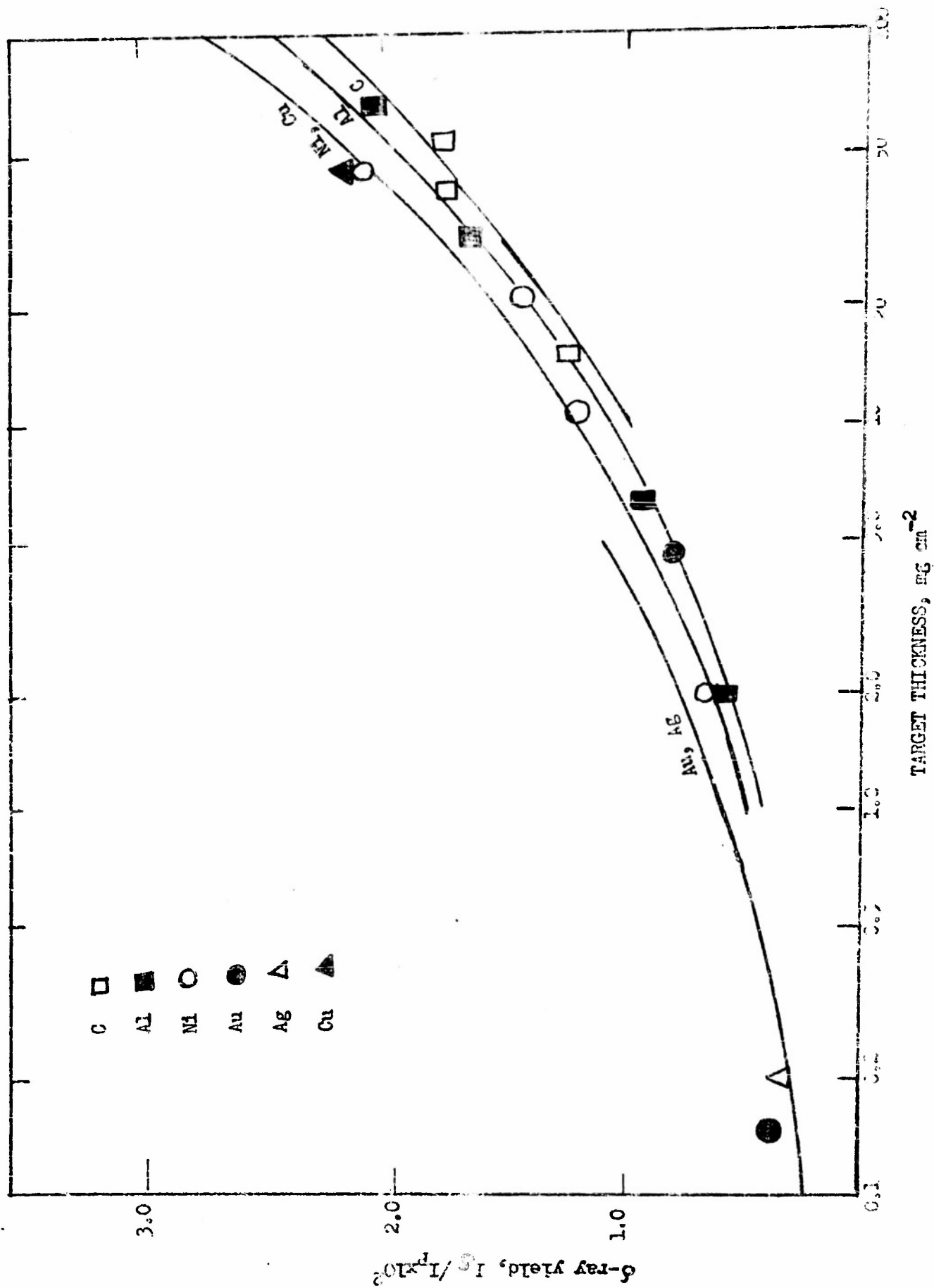


Fig. 6



#### IV. Theoretical Discussion

On the basis of a model involving several simplifying approximations, the delta ray yield expected theoretically from a target of specified atomic number and thickness may be computed. The assumptions are: (a) the electrons in the target can be treated as unbound; (b) the delta ray energies are much lower than the energy of the primary; and (c) a secondary created at a distance  $x$  from the surface of the target will emerge if its residual range is greater than  $x$ .

Under these conditions, the delta ray yield ( $\delta$ ) is given by

$$\delta = \int_0^{\ell} f(E) dx \quad (1)$$

where  $f(E)$  is the number of secondaries produced per unit path of the primary, with energy greater than  $E$ , the minimum energy necessary for escape from depth  $(\ell - x)$ , and  $\ell$  is the thickness of the target. Assuming the rate of energy loss of the secondaries to be given by

$$\frac{dE}{dx} = -\psi(E) \quad (2)$$

and changing the variable of integration in Equation (1) from  $x$  to  $E$ , we obtain

$$\delta = \int_0^{E_\ell} \frac{f(E)}{\psi(E)} dE \quad (3)$$

where  $E_\ell$  is the energy of an electron whose range is equal to  $\ell$ , and is obtained from

$$\ell = \int_0^{E_\ell} \frac{dE}{\psi(E)} \quad (4)$$

The rate of production of internal secondaries may be obtained, either from Møller's expression<sup>6)</sup> for the production of knock-on electrons, or from a purely classical calculation. Both yield

$$f(E) = Q_1/E \quad (5)$$

Here,  $\mu = mc^2$ , the rest energy of the electron, and

$$C = 2\pi N_0 r_0^2 \frac{Z}{A} = 0.3 \frac{Z}{A} \text{ gm}^{-1} \text{ cm}^2$$

where  $N_0$  is Avogadro's number,  $Z$  and  $A$  are the charge and mass numbers of the target material, and  $r_0 = \frac{e^2}{\mu}$  is the classical radius of the electron.

The rate of energy loss is given by the Bethe-Bloch expression

$$\psi(E) = \frac{Q_1^2}{E} \ln \frac{2E}{I} \text{ ev gm}^{-1} \text{ cm}^2 \quad (6)$$

(Relativistic effects are unimportant in the present case). Here, as is customary,  $I$  is assumed to be proportional to the atomic number of the target material,  $I = aZ$ . The final results are found to be extremely insensitive to the choice of the constant of proportionality, and for purposes of calculation,  $a$  is taken to be 11.5 ev.<sup>7)</sup>

Substituting (5) and (6) in (3) one obtains

$$\delta = \frac{I}{2\mu} \overline{Ei} \left( \ln \frac{2E}{I} \right) \quad (7)$$

where

$$\overline{Ei}(x) = \int_{-\infty}^x \frac{e^{-t}}{t} dt$$

and Equation (4) becomes

$$l = \frac{I^2}{4C\mu^2} \overline{E_i} \left( 2 \ln \frac{2E_i}{I} \right) \quad (8)$$

Solving (8) for  $l \sim \frac{2E_l}{I}$  and substituting in (7) one then obtains the delta ray yield as a function of the thickness and atomic number of the target.

From an analysis similar to that already outlined, one can determine the energy distribution of the emergent secondaries, and it is found that almost all of them have energies between 10 and 100 <sup>8)</sup> kev. Consequently, assumption (b) is valid, as is (a) for all but the most tightly-bound target electrons. Assumption (c) is not so well justified, since the path of an emerging secondary is in general longer than the distance from its point of origin to the surface, and the computed yields are consequently too high by about a factor of two. The ratio of the computed to the experimentally-determined yield is, however, substantially the same in all cases, indicating that the dependence of the delta ray yield on the thickness and atomic number of the target is correctly given by Equation (7).

The computed yields normalized to fit the experimental value for 46 mg cm<sup>-2</sup> Ni are plotted in Fig. 6. Theory and experiment are in agreement within the experimental uncertainties, except for the case of 5 mg cm<sup>-2</sup> Au. This discrepancy may be caused either by the stopping of an appreciable number of primaries (0.1 percent) or by the fact that the scattering of the secondaries has not been taken into account in the theory. Both of these effects would be more pronounced in a high Z material such as gold.

ACKNOWLEDGMENT

The authors wish to acknowledge the assistance of  
Mr. Arthur E. Smith in the experimental program.

### References

- 1) J. G. Trump and R. J. Van de Graaff, J. Appl. Phys. 18, 327 (1947); Phys. Rev. 75, 44 (1949).
- 2) B. L. Miller and W. C. Porter, Phys. Rev. 85, 391 (1952).
- 3) The ratio  $I_T/I_p$  is defined as positive when the sense of the current  $I_T$  corresponds to a net emission of electrons from the target, and negative when the number of electrons emitted is less than the number collected from other sources, per primary electron.
- 4) B. L. Miller, Rev. Sci. Inst. 23, 401 (1952).
- 5) S. Roberts, Rev. Sci. Inst. 10, 181 (1939).
- 6) C. Moller, Ann. d. Phys. 14, 531 (1932).
- 7) R. R. Wilson, Phys. Rev. 60, 749 (1941).
- 8) A lower limit to the delta ray energies has been determined by an independent method of observing the energy distribution of the low-energy secondary electrons, and no current of delta rays with energies less than 2 kev has been detected.  
R. A. Shatas, J. F. Marshall and M. A. Pomerantz, Phys. Rev. 94 (1954).

PUBLICATIONS AND PAPERS PRESENTED

M. A. Pomerantz

"Investigations of Secondary Electron Emission" - Office of Naval Research Conference on Surface Physics as Related to Electronics Phenomena, University of Missouri, May 25, 1951.

I. F. Patuf and M. A. Pomerantz

"Contact Potential Differences", Journal of The Franklin Institute 252, 239 (1951)

M. A. Pomerantz and J. F. Marshall

"Fundamentals of Secondary Electron Emission", Proceedings of the I.R.E., 39, 1367 (1951)

J. F. Marshall

"The Theory of Secondary Emission", Physical Review 88, 416 (1952)

J. F. Marshall

"Theory of Secondary Emission" - Twelfth Annual Conference on Physical Electronics, Massachusetts Institute of Technology, March 27, 1952

J. F. Marshall

"Theory of Secondary Emission" - Invited Paper, American Physical Society Meeting, Rochester, N. Y., June, 1953

R. A. Shatas, J. F. Marshall and M. A. Pomerantz

"Energy Distribution of Secondary Electrons Produced by 1.3 Mev Primary Electrons", American Physical Society Meeting, New York, N. Y., January, 1954

J. F. Marshall, M. A. Pomerantz and R. A. Shatas

"Secondary Emission From Metal Foils Bombarded by High Energy Electrons" - Fourteenth Annual Conference of Physical Electronics, Massachusetts Institute of Technology, March 25, 1954

M. A. Pomerantz, J. F. Marshall and R. A. Shatas

"Forward-Backward Ratio of Secondary Emission Produced by 1.3 Mev Electrons", American Physical Society Meeting, Washington, D. C., April, 1954

J. F. Marshall, R. A. Shatas, and M. A. Pomerantz

"Target-Thickness Dependence of Delta-Ray Emission Produced by 1.3 Mev Electrons", American Physical Society Meeting, Washington, D.C., April, 1954

R. A. Shatas, J. F. Marshall, and M. A. Pomerantz

"Emission of Energetic Secondary Electrons Produced by 1.3 Mev Electron Bombardment", Physical Review (In process of publication)

# CONTACT POTENTIAL DIFFERENCES

by  
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## CONTACT POTENTIAL DIFFERENCES \*

BY

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### 1. INTRODUCTION

The potential differences and charges acquired by dissimilar materials in contact are related to phenomena observed at the very beginning of the history of experimental electricity. Although there never was any doubt regarding the reality of the potential differences which could be produced between insulators such as amber, glass, wood, wool, leather, etc., the existence of a potential difference between metals has been a controversial issue.

This effect was discovered and first measured by Volta in 1797. Such well-known figures as C. E. Maxwell, W. Ostwald, O. Lodge, and others thought that the true contact potential between pure metals is negligible, of the order of magnitude of the Peltier effect, amounting to some hundredths of a volt at most. The observed magnitudes of several volts were attributed to impurities such as adsorbed gas layers or thin layers of electrolytes adhering to the metallic surfaces. It is only in relatively recent times that a decisive state has been reached. Notable contributions toward this end were the experiments of Coehn (1)<sup>4</sup> and of Perucca (2), who revealed that reproducible measurements could be made, and the theoretical treatments of Sommerfeld (3) and Eckart (4), who predicted the existence of contact potential differences of the observed order of magnitude from purely physical considerations. Thus, although it was originally assumed that the explanation of contact potential must be based upon a treatment of chemical equilibrium involving electrochemical theories such as those of Helmholtz and Nernst, it was finally realized that the subject with which this paper is concerned constitutes an exclusively physical effect.

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<sup>1</sup> Deceased; formerly, Physicist, Bartol Research Foundation of The Franklin Institute, Swarthmore, Pa.

<sup>2</sup> It was with great sorrow that the Bartol Research Foundation lost, through death, the services of Dr. Imre F. Patai in January, 1949. Although Dr. Patai had been with the Foundation for only six months, the warmth of his personality had endeared him in the hearts of all of us, and it is a happy comfort for us to know that this feeling was reciprocated. The present paper has been prepared by Dr. Martin A. Pomerantz on the basis of notes left by Dr. Patai at the time of his death, and while it is only the beginning of what would have been an extended development had he lived, it does form a valuable unit of accomplishment in itself. [W. F. G. Swann, Director, Bartol Research Foundation of The Franklin Institute.]

<sup>3</sup> Physicist, Bartol Research Foundation of The Franklin Institute, Swarthmore, Pa.

<sup>4</sup> The boldface numbers in parentheses refer to the references appended to this paper.



As in other phenomena of an allied nature, the surface conditions are of paramount importance. Minute traces of chemically active gases produce surface films which can modify the contact potential markedly. It is therefore not surprising that many discrepancies among the results of various investigators arose in the early work which did not utilize vacuum techniques. Even under the most carefully controlled conditions, reproducible results have not always been obtained.

Considerable confusion has arisen in the literature as a consequence of the many definitions adopted by different authors. For example, terms such as "contact potential," "Volta potential," "contact potential of the first kind," "contact potential of the second kind," "inner" or "outer Volta potential," etc., occur in various references. All of the aforementioned terms have been applied to the potential difference which exists at the point of contact of two metals. Furthermore, this terminology has been employed in the discussion of the contact potential between various pairs of the classes of solids defined by the nature of their electrical conductivity as ionic conductors, electronic conductors, or dielectrics. For example, Gysae and Wagener (5) defined four varieties as follows:

- (1) Electronic conductor-electronic conductor: "Galvani potential."
- (2) Electronic conductor-dielectric (vacuum between bodies): "Contact potential" when bodies are electrically connected; "charge potential" when bodies are insulated.
- (3) Electronic conductor ionic conductor: "Volta potential."

However, the most prevalent practice has been to denote the quantity measured by the various methods which will be described later as the *contact potential* or *Volta potential*.

The term "Galvani potential" has in general been relegated to the electrochemical phenomenon as distinguished from this purely physical effect. It symbolizes the supposed electrical potential *inside* a phase, and unfortunately, is an indefinite quantity. This so-called "internal potential" is the sum of the electrostatic potential outside a phase, and the electrostatic part of the work required to take electrons from the interior through the transition layer at the surface, to the point outside at which the electrostatic potential is measured. There are no known means of distinguishing between the electrostatic part of the work of extraction of an electron and the chemical part due to the difference in chemical environment of the electrons in the interior of the phase and outside.

## II. THEORY OF CONTACT POTENTIAL

### A. Fundamental Principles

The theory of electrical conductivity leads to the conclusion independently of experimental evidence that a potential difference should

exist between the interiors of two metals in contact even when their temperatures are equal. In the equilibrium state this is represented by the equation:

$$V_2 - V_1 = \frac{(\zeta_2 - \zeta_1)}{e}, \quad (1)$$

where  $\zeta$  is the Gibbsian thermodynamic potential of the electrons, designated as the Fermi energy at temperature  $T$ , and  $e$  is the electronic charge. The derivation of this fundamental relationship will be outlined later.

The quantity  $(V_2 - V_1)$  cannot be measured, however, owing to the fact that its magnitude depends upon the zero-point energies in the two metals. For free electrons, these energies may be regarded as equal to zero when the kinetic energies are zero. In this case  $\zeta_1$  and  $\zeta_2$  represent purely kinetic energies, and the internal field shifts the energy zero by an amount  $(\zeta_2 - \zeta_1)$  such that:

$$(\zeta_1 - eV_1) = (\zeta_2 - eV_2). \quad (2)$$

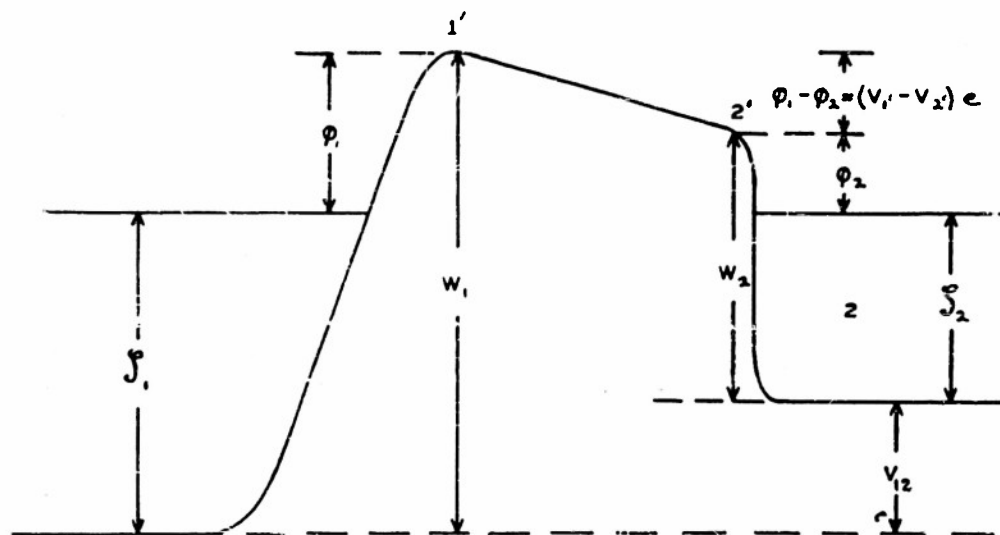


FIG. 1.

Although the internal field is not measurable, the contact potential, that is, the difference in potential between two points just outside each metal, is independent of the zero-point energies, and hence measurable. The situation is indicated in Fig. 1. Here  $-W_1$  and  $-W_2$  are the potential energies of an electron in the specified metal relative to a vacuum, whereas  $\phi_1$  and  $\phi_2$  represent the respective work functions. The potential difference between points 1' and 2', or the contact potential, is given by:

$$V_{2'} - V_{1'} = \frac{1}{e} [(W_1 - \zeta_1) - (W_2 - \zeta_2)] = - \frac{(\phi_2 - \phi_1)}{e}. \quad (3)$$

### B. Derivation Based Upon Free Electron Model

According to the usual connotation, a contact is described as a junction at which the distance apart between the bodies is comparable, at least in order of magnitude, with inter-atomic dimensions. It is entirely consistent with wave-mechanical principles for electrons to pass even across a relatively large gap at any temperature including absolute zero. The wave function will undergo total reflection at the surface of the first metal, but it is possible for penetration to occur into the second metal, with the amplitude of the transmitted wave decreasing exponentially.

It is evident that, in accordance with the above definition, two surfaces are in actual contact over a very limited region, and the major portions are separated by gaps many atomic dimensions wide. Of course, these gaps must be taken into account in any theory of the conduction of electricity.

Consider two metals as indicated in Fig. 1. Here, an exchange of electrons between 1 and 2 will occur. The current density  $j_{12}$  flowing from metal 1 to metal 2 may be expressed as follows (6):

$$j_{12} = 2\pi m \int_0^\infty T_{12}(E_x) dE_x \int_0^\infty f_1(E_1) dE_r; \quad (4)$$

similarly, the number of electrons passing from metal 2 to 1 per unit area per unit time is:

$$j_{21} = 2\pi m \int_0^\infty T_{21}(E_x) dE_x \int_0^\infty f_2(E_2) dE_r. \quad (5)$$

$E_x$  denotes that part of the kinetic energy which corresponds to the component of motion normal to the surface, while  $E_r$  signifies the portion associated with the parallel motion. Inasmuch as the principle of reversibility must be operative in a system of this type, the transmission coefficient  $T_{21}(E_{x_1})$  is equal to  $T_{12}(E_{x_1})$ . Hence

$$T_{21}(E_{x_1} + V_{12}) = T_{12}(E_{x_1}), \quad (6)$$

where  $V_{12}$  denotes  $(E_{x_1} - E_{x_2})$ , that is, the decrease in potential of an electron passing from metal 1 to 2.

From the above relationships:

$$j_{21} = 2\pi m \int_0^\infty T_{12}(E_x) dE_x \int_0^\infty f_2(E_1 + V_{12}) dE_r. \quad (7)$$

Hence the net flow in the direction  $1 \rightarrow 2$  per unit area per unit time is given by:

$$J = \frac{2\pi m}{h^3} \int_0^\infty T_{12}(E_x) dE_x \int_0^\infty [f_1(E_1) - f_2(E_1 + V_{12})] dE_r. \quad (8)$$

For equilibrium,  $J$  must vanish. This can occur only if in the latter equation:

$$f_1(E_1) = f_2(E_1 + V_{12}) = f_2(E_2). \quad (9)$$

Since

$$f_1(E_1) = \frac{2}{h^3 \epsilon \frac{(E_1 - \zeta_1)}{kT} + 1} \quad (10)$$

it is seen that, provided the two metals are at the same temperature, this condition can be fulfilled if:

$$E_1 - \zeta_1 = E_2 - \zeta_2 \quad (11a)$$

or

$$V_{12} = E_2 - E_1 = \zeta_2 - \zeta_1. \quad (11b)$$

This fundamental result was stated earlier in this section as Eq. 1.

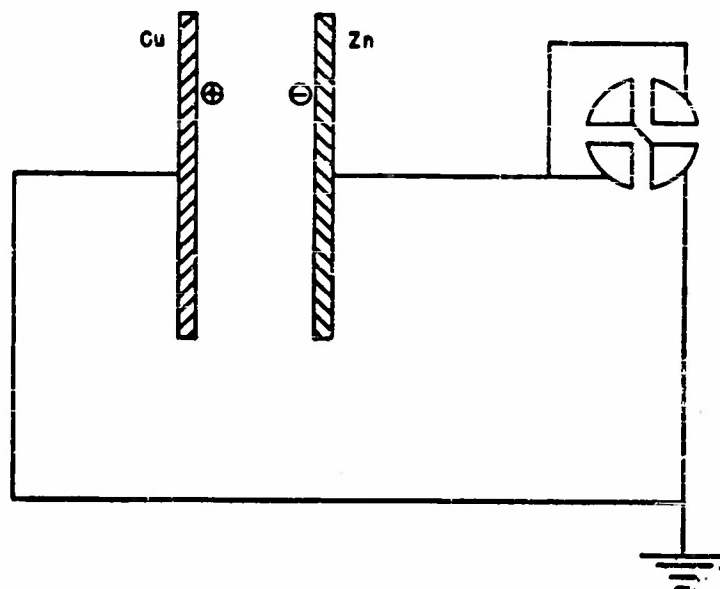


FIG. 2.

### III. METHODS FOR MEASURING CONTACT POTENTIALS

A large variety of methods has been employed for investigating this phenomenon. As is generally true in the case of effects which are dependent upon the surface conditions of the material under investigation, the results have often not been reproducible. In some instances, on the other hand, measurements conducted by different methods have yielded excellent agreement.

#### A. Ionization Method

The original experiments performed by Kelvin (7) utilized a technique which is exceedingly simple in principle. The method is repre-

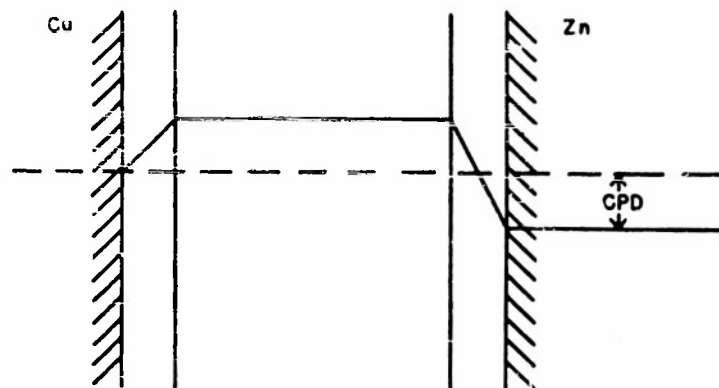


FIG. 3.

sented schematically in Fig. 2. One of the metals, copper in the example, is grounded, whereas the other metal with respect to which the contact potential is desired is placed adjacent and is connected to one of the pairs of quadrants of a quadrant electrometer. If a radioactive source is brought into the vicinity of the plates, the outer surfaces of the metals are essentially connected together, so that their potentials equalize. Consequently, a potential arises between the metals themselves. This is called the Volta potential difference. The nature of the potential distribution is indicated in Fig. 3. The potential is constant in the region between the plates, and decreases in a small transition region under the surfaces of both metals becoming again constant in the interiors. The fall in zinc is greater, indicating that it is negatively-charged with respect to copper.

It is apparent that it is essential to ionize only the air between the plates, and to avoid ionization elsewhere in the apparatus, in order to prevent the loss of charge to other objects. Greinacher (8) used a lead strip, on which was deposited a radioactive source, as one of the plates.

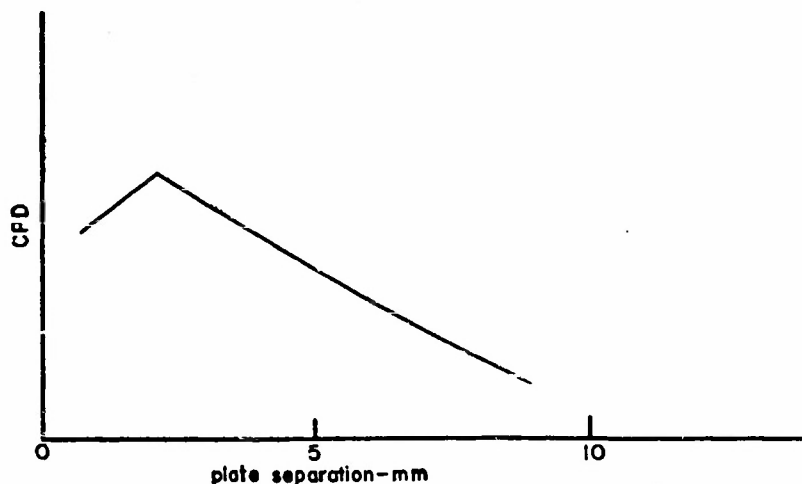


FIG. 4.

This permitted bringing the metals very close together and thereby reducing the irradiation of the surroundings. However, this does not completely solve the difficulty. Owing to the short range of the alpha particles, the magnitude of the electrometer deflection depends upon the separation of the plates. In order to utilize completely the ionizing potentialities of the source, the radiation proceeding from it should traverse a certain optimum thickness of air. Upon increasing the separation of the plates, the effect of recombination of ions enters, causing a subsequent decrease. As a consequence, a curve such as that shown in Fig. 4 is obtained. It was observed that the best separation is approximately 2 mm., for the tellurium source used. As a control upon the experiment, Greinacher also observed the resistance of the

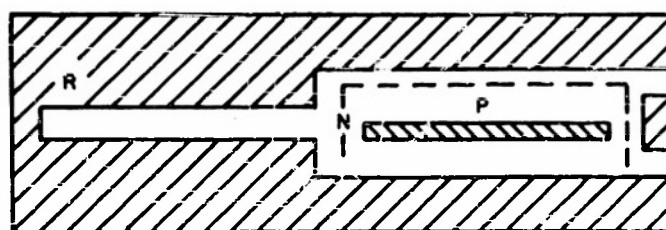


FIG. 5.

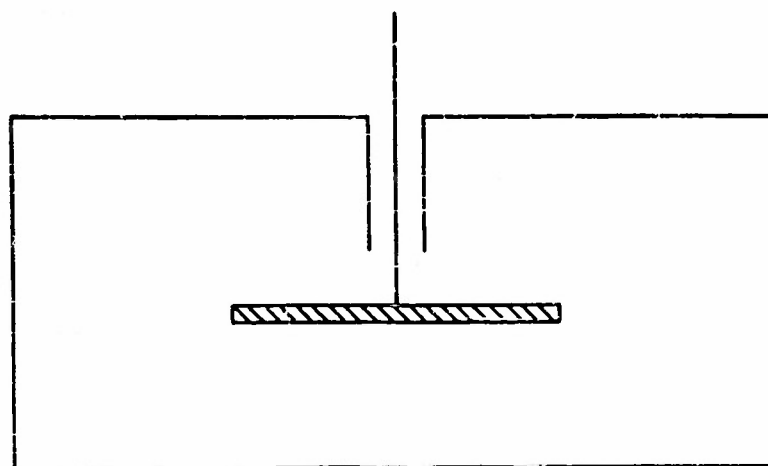


FIG. 6.

cell, to determine whether water droplets or other disturbances were operative.

K. T. Compton (9) improved the apparatus by using as one metal a wire net *N*, and as the other a plate *P* in a large lead container. The radium source was then situated at *R*. This device had the advantage that photoelectric measurements could also be conducted at the same time. Radiation of the surrounding region is here practically entirely avoided. The arrangement is illustrated in Fig. 5. In principle, the use of a third metal as a tank is not free from objections, inasmuch as

the potential difference of the metal under investigation with respect to lead might introduce errors. However, in practice, this does not appear to be significant. The values of the Volta potential thus determined seem to agree quite well with those obtained from photoelectric measurements, as may be concluded from the summary of Compton's results in Table I.

TABLE I.—*Comparison of Contact Potential Difference of Various Metals with Respect to Cu, as Determined by the Ionization and Photoelectric Methods (Ref. 9)*

	Al	Zn	Pb	Fe	Pt
Ionization Method	1.02	0.75	0.55	0.15	−0.11
Photoelectric Method	1.16	0.70	0.50	0.25	−0.14

J. J. McHenry (10) minimized the aforementioned possible source of error in his arrangement illustrated in Fig. 6. Here, the metal box

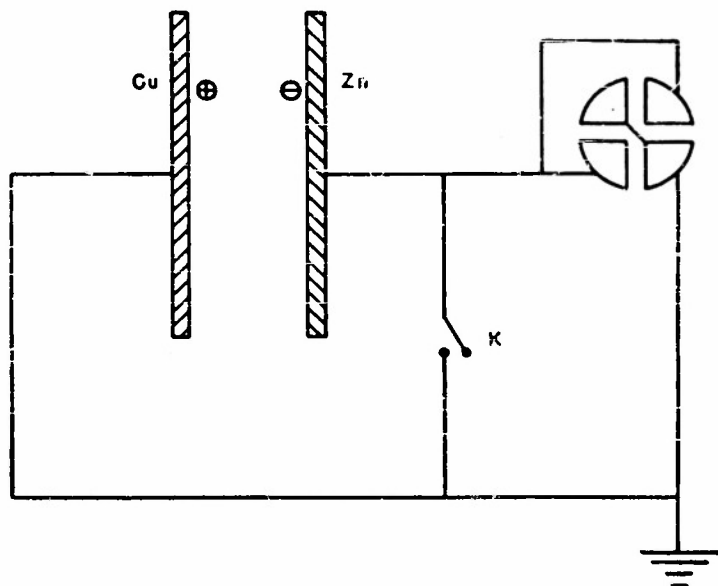


FIG. 7.

itself served as one electrode, and the second electrode was introduced through a very narrow orifice.

### B. Condenser Method

The arrangement originally employed by Kohlrausch (11) but usually designated as the Kelvin method, here is indicated schematically in Fig. 7. If the key *K* is closed, the metals themselves are connected rather than the surfaces of the metals as in the previous method. The potential distribution is then represented by Fig. 8. The potential now has the same height in both metals. In the transition regions, there is an increase which differs for the two metals, and consequently a drop

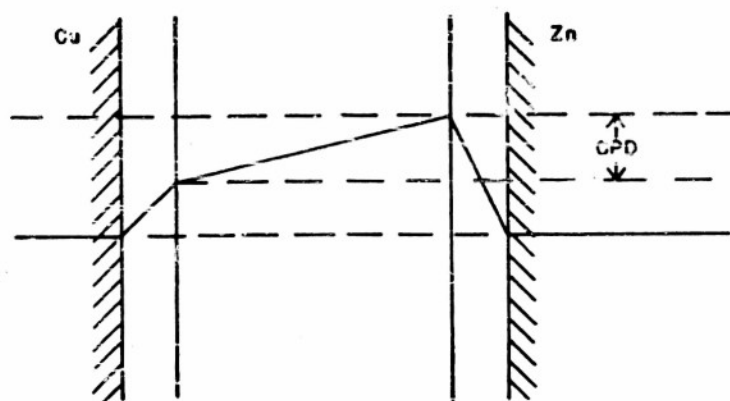


FIG. 8.

in potential occurs in the space between the surfaces. The electric field in the interspace is exactly that which would be produced by charging zinc positively with respect to copper. This method ostensibly leads to a Volta effect with reversed sign. The charge is then measured by varying the separation between the plates, thereby altering the capacitance. The measurement can be performed in various ways, although a null method is most satisfactory.

As a consequence of the fact that, in the arrangement of Fig. 7, a potential  $V$  arises when the key  $K$  is closed, the condenser comprising the two plates is charged to an amount  $Q = C_1 V$ . When the Zn side is isolated by opening  $K$ , the entire charge resides thereon. Upon increasing the spacing between the two plates, the charge distributes itself between the parallel plate condenser now having the capacitance

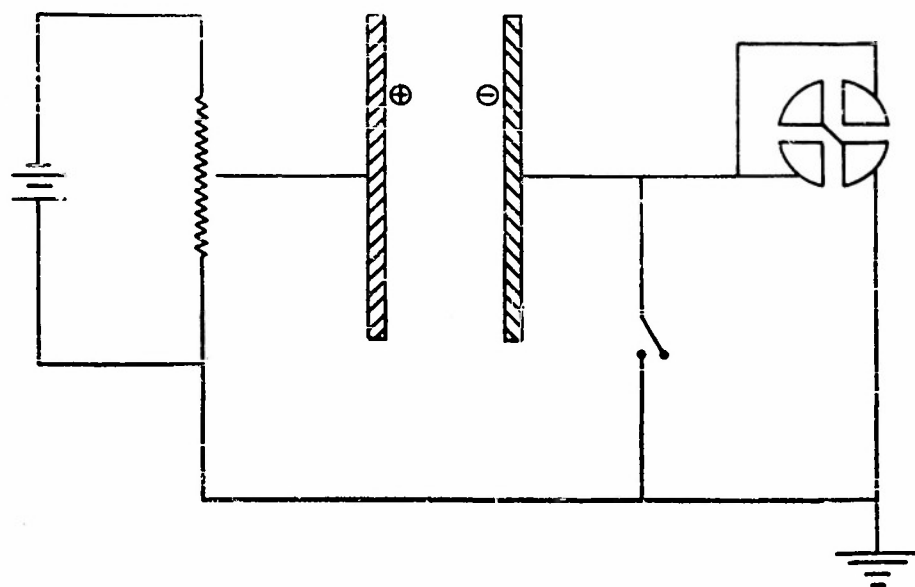


FIG. 9.



$C_2$ , and the electrometer system and leads having capacitance  $C$ . Hence:

$$Q = V'(C_2 + C), \quad (12)$$

where  $V'$  is the potential measured by the electrometer. Consequently:

$$V = V' \frac{(C_2 + C)}{C_1}. \quad (13)$$

In order to avoid the necessity for determining  $C_1$ ,  $C_2$ , and  $C$ , the customary procedure involves the calibration of the electrometer by the application of known potentials. The most satisfactory procedure is a null method first utilized by Kelvin (7). Here the potential  $P$  is applied by means of a potentiometer, as is indicated in Fig. 9. This method is rather time-consuming, and even modifications such as the plotting of deflection *vs.* bucking potentials proposed by Ende (12) are relatively cumbersome.

The principal problem associated with the condenser method is the necessity for providing a mechanism for altering the plate separation.

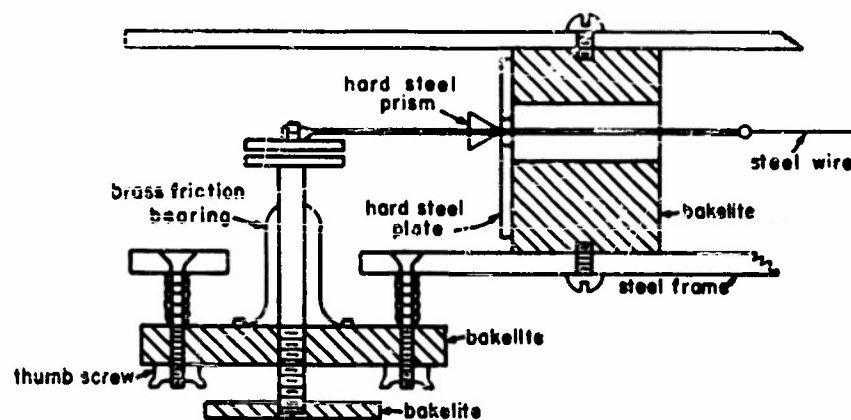


FIG. 10.

Initially, rather crude methods sufficed. Kelvin, for example, merely separated the plates by hand, whereas Kohlrausch provided a silk thread suspension. The most precise determinations up to his time, as evidenced by the reproducibility of the results, were obtained by Conrad (13) who constructed what was then a relatively complicated system involving a lever and a support. It is evident that none of the aforementioned arrangements is adaptable to measurements in vacuum. However, such experiments can easily be accomplished by introducing the required motion into the vacuum system by means of magnetically-actuated moving parts.

A significant improvement upon the classical Kelvin method was introduced by Zisman (14). The electrometer in Fig. 9 is replaced by the input to an audio-frequency amplifier, and the capacitance of the condenser is varied periodically. An audio-frequency signal is then

heard until the applied potential difference balances the contact potential. The measurement consists merely in balancing a resistance until no signal is heard, and it can be carried out in a few seconds, whereas the older method was slow and tedious. The vibrating condenser arrangement, shown in Fig. 10, involves a steel piano wire against the middle of which an air blast is directed from a small nozzle. One end of the wire is fixed while the other end rocks a metal rod threaded through a triangular knife-edged prism which rests upon a steel plate. The moving plate of the condenser is fastened to the other extremity of the rod. The method originally permitted the measurement of contact potentials with certainties up to one-thousandth of a volt in but a few seconds of manipulation, and this can probably be improved by modification of the amplifier.

This principle would be very valuable for studies of variations with orientation of the contact potential between the faces of single metal crystals and some standard metal surface, or in the study of rapid changes with time of the contact potential between pairs of newly prepared surfaces. Furthermore, information regarding the uniformity of the metallic surface is provided by the fact that a zero sound minimum is obtained only with a uniform surface. In a modification developed by Rosenfeld and Hoskins (15) the condenser plate was vibrated by 60-cycle current.

The condenser method has many advantages, certainly as compared with the ionization method which has the fundamental disadvantage that the measurements depend upon the resistance of the ionized air. Obviously the condenser method can be utilized in vacuum, and furthermore the sensitivity is considerably higher. The principal precaution, aside from the usual requirements regarding vacuum and degassing practice, is concerned with the avoidance of the accumulation of spurious charges on insulating bodies near the specimens under investigation. The condenser method, in principle, is the only one which actually measures contact potential directly as compared with other procedures which will be discussed later. Its most unfavorable aspect is the necessity for moving the electrode, although, as mentioned above, modern techniques are readily adaptable to this purpose.

### C. *The Photoelectric Effect*

#### 1. *Field Between Electrodes*

The photoelectric effect merely provides a source of electrons in this instance. The motion of these electrons is then determined by the potential distribution in the region between the surface from which they were emitted and a second metal nearby.

(a) *Curve Displacement Method.* In this case, the applied potential  $P$  and the contact potential  $V$  are superimposed. Thus, the potential between the electrodes is given by  $V_1 = P + V$  with a given anode,

and  $V_1' = P + V'$  with another anode. It is evident that with the same applied voltage, the effective potential differs for different metals. Consequently, as may be seen in Fig. 11, a parallel displacement of the *photocurrent vs. applied potential* curve results. Inasmuch as zinc is positive with respect to copper, the curve obtained with the former material appears on the left.

K. T. Compton (9), utilizing a plate cathode surrounded by a grid anode, measured contact potentials by both the ionization method and by this method, and obtained the results listed in Table I.

(b) *Saturation Current Method.* The difficulties associated with the procedure described above are circumvented in the saturation current method. Here the cathode is surrounded by an anode and conditions are established such that no field exists in the interspace. Electrons leave the cathode with all possible velocities between zero and a certain

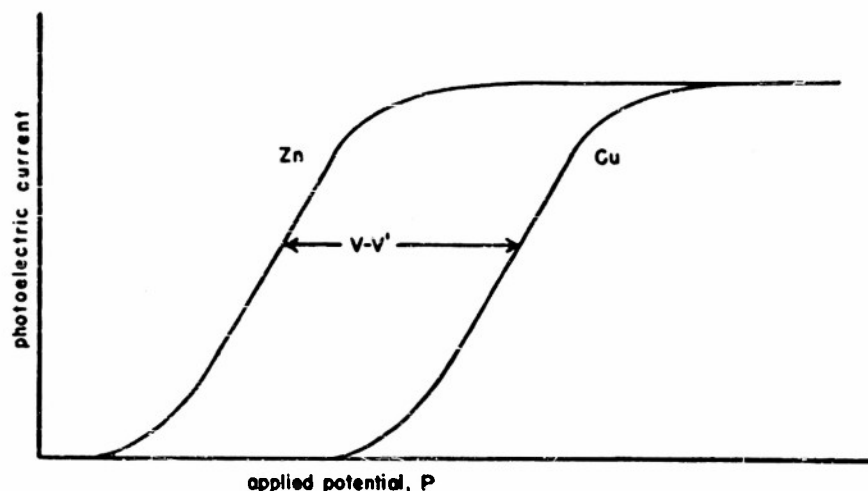


FIG. 11.

maximum. However, the precise velocity distribution plays no role, inasmuch as all electrons emanating from the cathode with finite velocity must reach the anode owing to the absence of an interelectrode field. Consequently the photoelectric current must first exhibit a saturation value when the true potential becomes equal to zero. As the potential between the electrodes decreases from cathode to anode, some of the electrons are repelled. The actual potential is equal to zero only when the applied potential is equal to the contact potential, and it is evident that, in principle, the contact potential corresponds directly to the value of applied voltage at which saturation current occurs.

Measurements of this type (16, 17, 18, 19) are usually performed in a glass envelope having an evaporated metallic layer, for example, silver, which serves as anode. The cathode may be in the form of a foil or another evaporated layer located as near the center of the anode as possible. Light is admitted through a port in the anode, and an opening

must be provided for introducing the specimen. Owing to the latter factors, the vessel is not completely closed, hence a rounding of the saturation curve rather than a sharp break is observed in practice. Extrapolation is required for determining the voltage at which saturation occurs, as may be seen in Fig. 12. Teichmann (20) reports agreement between measurements obtained with this method and with the condenser method.

Inasmuch as measurements of the magnitude of the saturation current are obtained in this procedure, some control is maintained over the state of degassing of the surface.

(c) *The Photoelectric Yield.* It has been shown (21) that the Voltaic series corresponds with the arrangement of metals according to their photoelectric yield. However, quantitative determinations of the latter

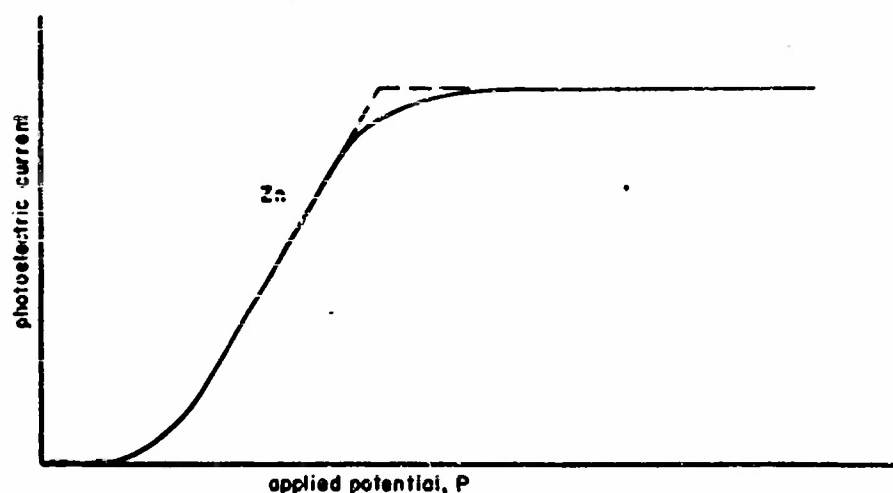


FIG. 12.

factor require knowledge of the photocurrent, the surface area, the light intensity and spectral distribution, the absorption in quartz windows, etc. The latter two characteristics are difficult even to hold constant, and so this method does not seem very practicable as a means of determining the contact potential.

## 2. Work Function

(a) *Long Wave Length Limit.* The well-known photoelectric equation of Einstein is:

$$V = \frac{h\nu}{e} - \varphi. \quad (14)$$

$V$  represents the value of applied potential such that no photoelectrons are emitted. When  $V = 0$ ,  $\nu = \nu_0$  and  $\varphi = \frac{h\nu_0}{e}$ . It is thus assumed that  $V$  can be determined precisely. Presumably, in accordance with

Eq. 3, the contact potential could be obtained directly from a comparison of the work functions as determined in this manner. However, in practice, the situation is not so clean-cut. Actually, it is found that  $\varphi$  can be represented as the sum of two terms  $p$  and  $q$ , of which the former relates to the contact potential, and the latter represents a remainder. Although according to experimental indications  $q$  has the same value for all metals, the explanation for its existence is not well understood. The empirical approach makes use of the following relationships:

$$V_1 = \frac{h\nu}{e} - p_1 - q_1 \quad (15a)$$

$$V_2 = \frac{h\nu}{e} - p_2 - q_2 \quad (15b)$$

The value of applied voltage  $P_1$  for which no photocurrent is observed is then determined. Now:

$$V_1 = P_1 - (p_1 - p_0), \quad (16)$$

where  $p_1 - p_0$  is the contact potential between cathode 1 and anode 0. Furthermore:

$$q_1 = \frac{h\nu}{e} - P_1 - p_0 \quad (17a)$$

and

$$q_2 = \frac{h\nu}{e} - P_2 - p_0. \quad (17b)$$

If the external potential necessary to produce cutoff can be regarded as constant for different cathodes and the same anode,  $P_1 = P_2$  and hence  $q_1 = q_2$ . However, the general ignorance regarding the physical identification of  $q$  makes this method very unsatisfactory.

The measurement of the long-wavelength limit is accurate only to within several per cent. Inasmuch as values of the work function usually range between 2-6 volts, the inaccuracies amount to some tenths of a volt, which is of the order of magnitude of the Volta effect. In view of the fact that two such values are required for the determination of contact potential, the limitations of the method are apparent.

Representative values obtained by Richardson and Compton (17) using both the saturation-current method and photoelectric threshold determinations are given in Table II.

TABLE II.—Comparison of Contact Potential Measurements, in Volts, Obtained with Respect to Platinum by Two Different Methods (Ref. 17)

	Cu	Bi	Sn	Zn	Mg	Al	Na
Saturation-current Method	0.13	0.35	0.62	0.90	1.05	1.2	2.4
Long Wavelength Limit	0.30	0.64	0.64	0.85	1.00	1.31	2.2

### D. Thermionic Emission Methods

These methods are similar to the photoelectric measurements in that one metal of a pair under investigation emits electrons, in this instance thermionically. The principal advantage is that the materials under investigation may be carefully degassed under vacuum conditions, particularly if the specimens are fabricated in the form of wire filaments.

#### 1. Field Between the Electrodes

The remarks in Section III-C are equally applicable here, inasmuch as the mode of production of the electrons is not a pertinent factor. The method involves the observation of the displacement of the characteristic *current vs. voltage* curve of a vacuum tube.

(a) *Diode Method.* The saturation-current method was originally used by Rotlie (22), Germer (23), and Reynolds (24). In their experiments, a filament was completely surrounded by the anode, as in the corresponding photoelectric technique. From the *current vs. voltage* curve, the applied potential  $P$  necessary to produce saturation is determined. This, of course, corresponds to zero effective voltage, and hence to the contact potential. It is a relatively simple matter to compare the contact potential of different anodes with respect to a fixed cathode.

Oatley (25) determined  $V_1 = V + P$  by measuring the value of the axial magnetic field which would just prevent the passage of electrons from filament to anode in a cylindrical diode. An analysis depending upon the relation between anode voltage and critical magnetic field originally deduced by Hull (26) for the magnetron, and requiring several approximations and corrections for departures from theoretical conditions owing to the absence of a sharp cutoff, permits the calculation of the desired quantity from the experimental data. The error of the determinations thus made is  $\pm 0.02$  volts.

The curve-shift method is superior to any of the aforementioned. In various forms, it was initially used independently and simultaneously by Mönch (27), Langmuir and Kingdon (28), and Patai (29, 30, 31, 32). The simplest arrangement utilizes a filament and a plate, the latter being replaceable by another specimen. The *current vs. voltage* curves

TABLE III.—Comparison of Contact Potential Difference Between Cu and Ni, as Measured Successively by the Condenser and Saturation-Current Methods (Ref. 27)

Volts	Method
0.26	Condenser
0.20	Saturation-current
0.22	Condenser
0.24	Saturation-current
0.22	Condenser
0.22	Saturation-current

corresponding to the various anodes are then plotted, and the parallel shift corresponds to the contact potential between the two anodes. Mönch has compared this method with the condenser method and, as may be seen in Table III, a series of measurements alternately performed on a given specimen are in good agreement.

(b) *Triode Method.* The three-electrode tube may be utilized in several ways. One technique involves the measurement of the contact potential between the grid and anode, with the filament serving merely as a source of electrons. It is necessary to provide for the control of effects such as a potential drop across the filament, and the temperature of the filament. As is indicated in Fig. 13, the grid is connected directly to the cathode, and the variable voltage  $P$  is applied between the grid and the anode. The shift in the  $V$ - $I$  curve is then observed. Either the grid or the anode may be changed, and the electrodes may be in the form of plates or cylinders.

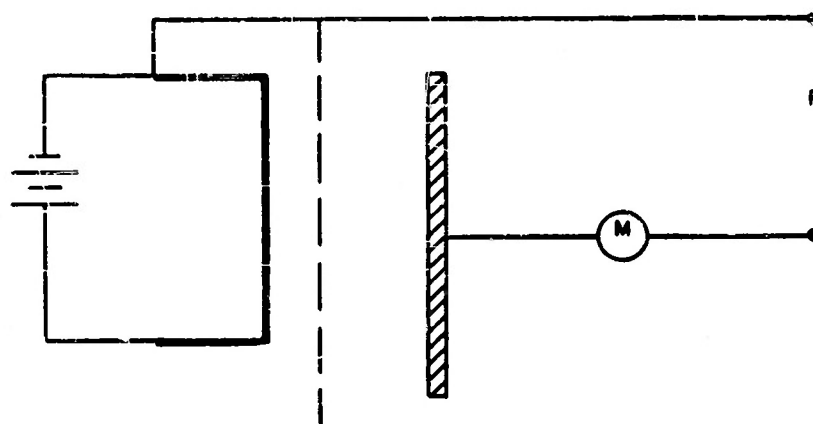


FIG. 13.

The most advantageous method for many applications is that originated by one of the authors (29, 30, 31, 32). No mechanical system is required for introducing motion into the vacuum tube. Careful degassing of the specimens can be accomplished, and sources of error arising from inhomogeneous field distributions are minimized by the concentric electrode arrangement without the introduction of guard electrodes.

The procedure consists of the determination of the characteristic curve of a three-electrode tube. This is measured first with a grid of the metal under investigation, and then again after a uniform layer of another metal has been coated thereon. In the first case, the characteristic curve is governed by the contact potential difference between the filament and the base metal of the grid, and in the second by that between the unchanged filament and the coated grid. The difference between the two cases manifests itself as a parallel shift of the characteristic curve, and the amount of the displacement constitutes a measure

of the contact potential between the grid base metal and the evaporated metal layer.

The shift is to the left, that is, toward negative values of grid voltage, if the grid is covered in the second instance with a metal for which the work function is smaller than for the base metal. In all of the experiments utilizing this method, sodium was employed as the covering applied to various bases to serve as a reference metal. In the first place, this metal can be introduced into an evacuated tube in a very pure state, by a method developed by one of the writers (33). Secondly, inasmuch as the work function for sodium is considerably smaller than that for the grid materials, an observable effect is always produced. Finally, the reference layer of sodium can easily be evaporated by heating the grid. Thus, the reproducibility of the measurements may

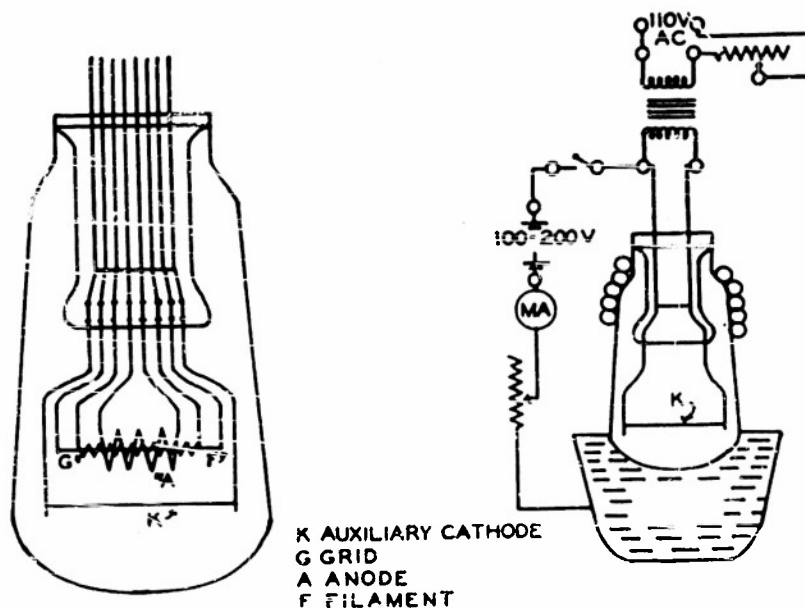


FIG. 14.

FIG. 15.

readily be checked by alternately glowing the spiral grid while the envelope is cooled, taking data, and then repeating after the glass envelope has been heated to recoat the grid. Figure 14 indicates the construction of the experimental tube. The grid *G*, as well as the spiral anode *A* of the triode, has two leads to permit heating directly by electric current. An auxiliary cathode *K* serves as the source of electrons for the electrolytic introduction of sodium into the tube. The envelope is constructed of soft lead-free glass. Usual vacuum precautions and procedures are observed in the preparation of the tube which is finally sealed off under conditions such that the residual pressure is less than  $10^{-8}$  mm. of Hg.

Sodium is introduced into the tube by an electrolytic process which is represented in Fig. 15. Any sodium salt may be used, although



$\text{NaNO}_2$  has the advantage of a low melting point. The bottom of the experimental tube is immersed in the molten salt, while the upper portion is surrounded by a cooling coil. A potential of the order of 100 to 200 volts is applied between the auxiliary cathode  $K$  and the salt. Currents of about 5 to 15 milliamperes flow during the process, and after 4 to 5 minutes the cooled walls of the tube become coated with a metallic mirror-like layer of sodium.

The characteristic curve (plate current *vs.* grid voltage) of the triode prepared in this manner is then obtained with at least two different

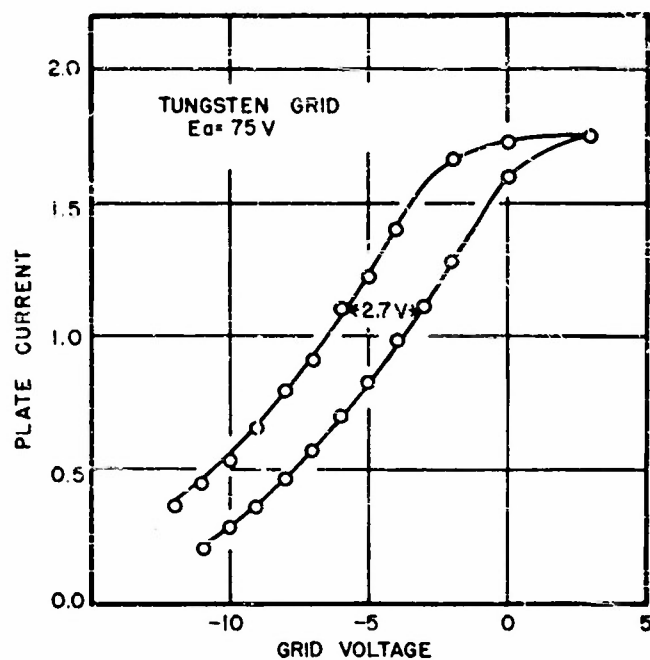


FIG. 16.

anode voltages. The shift of the characteristic curve corresponding to the clean grid with and without the sodium layer turns out to be completely independent of the anode voltage. The curves of Fig. 16 are typical of those obtained with this arrangement. The results of measurements on various materials are summarized in Table IV. The

TABLE IV.—*Measured Values of Contact Potential Differences of Various Metals with Respect to Na (Ref. 31)*

Mo	W	Fe	Ni	Pt	Cu
2.0	2.7	1.4	2.45	2.1	2.05

contact potential differences with respect to sodium are in good agreement with values deduced from the differences of work functions determined thermionically and photoelectrically in the case of the particular metals investigated.

## 2. Work Function

The theoretical discussion in Section II leads to the conclusion that the contact potential between two metals is equal to the difference between their work functions. This would suggest that the measurement of work functions should provide a satisfactory method for evaluating contact potentials. However, the difficulties associated with accurate work function determinations are well known, and the limitations mentioned in the discussion of photoelectric measurements are equally applicable here.

## IV. CONCLUDING REMARKS

It has not been the purpose of the present paper to provide an extensive survey of the entire subject of contact potentials. On the contrary, attention has been confined to the fundamental aspects of this subject, and particularly to a critical consideration of the experimental methods of determining contact potential differences. In conformity with this point of view, extremely small temperature effects which are known to occur, but which are orders of magnitude smaller than contact potentials (34, 35) have not been mentioned. Furthermore, the additional complications inherent in the nature of the contact between a metal and a semi-conductor have been avoided by restricting the discussions to metals only.

This policy has its inception in the desire to investigate the feasibility of employing contact potential measurements as a tool, in conjunction with other types of observations such as secondary-electron emission, thermionic emission, and the photoelectric effect, for arriving at a more profound understanding of certain properties of solids. Perhaps the most interesting theoretical problems in this field relate to the observation originally made by Rose (36, 37) and later by Kurzke and Rottgardt (38) that the contact potential depends upon crystal orientation in the case of single crystals.

## REFERENCES

- (1) A. COHEN, *Hand. d. Phys.*, Vol. XIII, p. 332 (1928).
- (2) E. PERUCCA, *Atti del Congresso Como* (1927).
- (3) A. SOMMERFELD, *Zeits. f. Phys.*, Vol. 47, p. 1 (1928).
- (4) C. ECKART, *Zeits. f. Phys.*, Vol. 47, p. 38 (1928).
- (5) B. GYSAE AND S. WAGENER, *Zeits. f. Phys.*, Vol. 110, p. 145 (1938).
- (6) J. FRENKEL, "Wave Mechanics," Oxford, The Clarendon Press, 1932, p. 244.
- (7) LORD KELVIN, *Phil. Mag.*, Vol. 46, p. 82 (1898).
- (8) H. GREINACHER, *Ann. d. Phys.*, Vol. 16, p. 709 (1905).
- (9) K. T. COMPTON, *Phil. Mag.*, Vol. 23, p. 579 (1912).
- (10) J. J. MCHENRY, *Phil. Mag.*, Vol. 3, p. 857 (1927); *loc. cit.*, Vol. 8, p. 474 (1930).
- (11) R. KOHLRAUSCH, *Pogg. Ann.*, Vol. 82, p. 1 (1851).
- (12) W. ENDE, *Phys. Zeits.*, Vol. 30, p. 477 (1929).
- (13) H. CONRAD, *Sitz. d. Wien. Akad.*, Vol. 122, p. 35 (1913).
- (14) W. A. ZISMAN, *Rev. Sci. Instr.*, Vol. 3, p. 368 (1932).
- (15) S. ROSENFELD AND W. M. HOSKINS, *Rev. Sci. Instr.*, Vol. 16, p. 343 (1945).

- (15) P. LENARD, *Ann. d. Phys.*, Vol. 8, p. 149 (1922).
- (17) O. W. RICHARDSON AND K. T. COMPTON, *Phil. Mag.*, Vol. 24, p. 575 (1912).
- (18) L. PAGE, *Am. Journ. Sci.*, Vol. 36, p. 501 (1913).
- (19) P. LUKIRSKY AND S. PRILEZAEV, *Zeits. f. Phys.*, Vol. 49, p. 236 (1928).
- (20) H. TEICHMANN, *Ann. d. Phys.*, Vol. 1, p. 1069 (1929).
- (21) J. ELSTER AND H. GEITEL, *Ann. Wied.*, Vol. 43, p. 225 (1891).
- (22) H. ROTHE, *Zeits. f. Techn. Phys.*, Vol. 6, p. 633 (1925).
- (23) L. H. GERMER, *Phys. Rev.*, Vol. 25, p. 795 (1925).
- (24) N. B. REYNOLDS, *Phys. Rev.*, Vol. 35, p. 158 (1930).
- (25) C. W. OATLEY, *Proc. Roy. Soc.*, Vol. 155, p. 218 (1936).
- (26) A. W. HULL, *Phys. Rev.*, Vol. 18, p. 31 (1921).
- (27) G. MÖNCH, *Zeits. f. Phys.*, Vol. 47, p. 522 (1928).
- (28) I. LANGMUIR AND H. K. KINGDON, *Phys. Rev.*, Vol. 34, p. 129 (1939).
- (29) I. PATAI, *Phys. Rev.*, Vol. 35, p. 145 (1929).
- (30) I. PATAI, *Zeits. f. Phys.*, Vol. 59, p. 697 (1929).
- (31) M. FORRO AND I. PATAI, *Zeits. f. Phys.*, Vol. 63, p. 444 (1930).
- (32) I. PATAI, *Mat es Fizikai Lapok*, Vol. 38, p. 62 (1931).
- (33) M. FORRO AND I. PATAI, *Zeits. f. Techn. Phys.*, Vol. 12, p. 256 (1931).
- (34) G. MÖNCH, *Zeits. f. Phys.*, Vol. 90, p. 433 (1934).
- (35) D. B. LANGMUIR, *Phys. Rev.*, Vol. 47, p. 813 (1935).
- (36) B. A. ROSE, *Phys. Rev.*, Vol. 44, p. 585 (1933).
- (37) H. E. FARNSWORTH AND D. A. ROSE, *Proc. Nat. Acad. Sci.*, Vol. 19, p. 777 (1933).
- (38) H. KURZKE AND J. ROTTGARDT, *Zeits. f. Phys.*, Vol. 100, p. 718 (1936).

#### ADDITIONAL BIBLIOGRAPHY

- R. A. MILLIKAN, "Distinction between Intrinsic and Spurious Contact EMF's and Absorption of Radiation by Metals in Quanta," *Phys. Rev.*, Vol. 18, pp. 236-44 (1921).
- E. PERUCCA, "Contact Potential Difference," *Acad. Lincei, Atti*, Vol. 30, pp. 54-57 (1921).
- A. COEHN AND A. LOTZ, "Contact Electricity in High Vacuo," *Zeits. f. Phys.*, Vol. 54, pp. 242-63 (1921).
- O. W. RICHARDSON AND F. S. ROBERTSON, "Effect of Gases on the Contact EMF between Metals at Different Temperatures," *Phil. Mag.*, Vol. 43, pp. 162-74 (1922).
- J. A. V. BUTLER, "Relation Between Metal Contact Potentials and the Peltier Effect," *Phil. Mag.*, Vol. 48, pp. 746-52 (1924).
- E. DOWLING, "Contact Electromotive Force between Two Dissimilar Metals," *Phys. Rev.*, Vol. 25, pp. 812-25 (1925).
- J. E. SCHRADER, "Effect of Heat Treatment on the Contact Potential Difference of Ni and Cu," *Phys. Rev.*, Vol. 25, p. 249 (1925).
- P. H. DOWLING, "The Contact EMF between the Solid and Liquid Phases of the Same Metal and between Outgassed Surfaces of Two Dissimilar Metals," *Phys. Rev.*, Vol. 25, pp. 812-25 (1925).
- W. H. RODEBUSH, "Thermal Equilibrium of Electrons in Metals: Contact Potentials and Thermoelectric Force," *Chem. Rev.*, Vol. 4, pp. 255-70 (1927).
- G. MÖNCH, "Measurements of Contact Potential between Metals in Vacuo," *Zeits. f. Phys. Chem.*, Vol. 34, pp. 98-103 (1928).
- E. DENINA, "Contact Electromotive Force," *Gazz. Chim. Ital.*, Vol. 58, pp. 160-77 (1928).
- J. FRENKEL, "Elementary Theory of Magnetic and Electrical Properties of Metals at Absolute Zero," *Zeits. f. Phys.*, Vol. 49, p. 31 (1928).
- I. F. BATES, "A Review on Contact Potential," *Science Progress*, Vol. 23, pp. 205-11 (1928).
- H. E. FARNSWORTH AND V. H. GOERKE, "Distinction between Contact Potential Effects and True Reflection Coefficients for Low-Velocity Electrons," *Phys. Rev.*, Vol. 36, pp. 119-74 (1930).
- E. DUBOIS, "The Volta Effect," *Annales de Physique*, Vol. 14, pp. 627-725 (1930).

- G. MÖNCH, "Comparison of Two Methods for Determining the Contact Potential between Two Metals," *Zeits. f. Phys.*, Vol. 65, pp. 233-43 (1930).
- G. N. GLASOE, "Contact Potential Difference between Fe and Ni and Their Photoelectric Work Functions," *Phys. Rev.*, Vol. 38, pp. 1490-6 (1931).
- O. SCARPA, "EMF in Closed Metallic Circuits at Uniform Temperature," *Zeits. f. Phys. Chem.*, Vol. 156, pp. 225-26 (1931).
- W. D. HARKINS AND H. E. BOWERS, "Spurious Contact Potentials and 'Trapped' Electrons," *Phys. Rev.*, Vol. 38, p. 1918 (1931).
- M. ANDAUER AND E. LANGE, "Relationship between Galvani Potential, Volta Potential and Adsorption of Ions Which Define the Potential," *Zeits. f. Phys. Chem.*, Vol. 156, pp. 241-57 (1931).
- R. FÜRTH, "Investigations on Contact Potentials. III. The Theory of the Contact Potential," *Zeits. f. Phys.*, Vol. 68, pp. 735-57 (1931).
- W. A. ZISMAN AND H. G. YAMINS, "Contact Potential of Zinc Crystals," *Physics*, Vol. 4, pp. 7-9 (1933).
- G. MÖNCH AND S. STECHHÖFER, "Thermoelectric and Volta Potentials of Cuprous Oxide," *Zeits. f. Phys.*, Vol. 84, pp. 59-65 (1933).
- P. I. LUKIRSKY, "Work Function and Photoelectric Properties of Metals," *Phys. Zeits. d Sowjetunion*, Vol. 4, pp. 212-38 (1933).
- G. MÖNCH, "I. Contact Potential, Energy of Emergence and Thermoelectrical Potential. The Relation between Energy of Emergence and Contact Potential," *Erlianger Ber.*, Vol. 65, pp. 191-201 (1934).
- G. MÖNCH, "II. The Relation of the Contact Potential to the Condition of Strain of a Metal Surface," *Chem. Zentr.*, Vol. 2, p. 20 (1935).
- F. ODORE, "Volta and Peltier Effects," *N. Cimento*, Vol. 12, pp. 273-84 (1935).
- P. A. ANDERSON, "The Contact Difference of Potential between W and Ba. The External Work Function of Ba," *Phys. Rev.*, Vol. 47, pp. 958-64 (1935).
- A. L. REIMANN, "Contact Potential Difference between Clean and Oxygenated W," *Phil. Mag.*, Vol. 20, pp. 594-607 (1935).
- R. M. BOWIE, "This Matter of Contact Potential," *Proc. I.R.E.*, Vol. 24, pp. 1501-13 (1936).
- P. A. ANDERSON, "Contact Potential Difference between Silver and Barium. External Work Function of Silver," *Phys. Rev.*, Vol. 49, pp. 326-23 (1936).
- D. B. LANGMUIR, "Contact Potential Measurements on Tungsten Filaments," *Phys. Rev.*, Vol. 49, pp. 428-35 (1936).
- R. C. L. BOSWORTH, "Contact Potentials. Evaporation of Sodium Films," *Proc. Roy. Soc.*, Vol. 162, pp. 32-49 (1937).
- R. C. L. BOSWORTH AND E. K. RIDEAL, "Studies in Contact Potentials. The Condensation of Potassium and Sodium on Tungsten," *Proc. Roy. Soc.*, Vol. 162, pp. 1-31 (1937).
- H. J. PLUMLEY, "Contact Potential for Metals Immersed in a Dielectric and Conduction of Electricity by Liquid Dielectrics," *Phys. Rev.*, Vol. 52, p. 140 (1937).
- E. PERUCCA, "Volta Effect in Vacuo," *N. Cimento*, Vol. 14, pp. 310-313 (1937).
- O. SCARPA AND C. ROSSI, "Volta Effect in Solid Metallic Alloys," *Atti Accad. Lincei*, Vol. 27, pp. 57-62 (1938).
- O. SCARPA, "Recent Work on Voltaic EMF," *Ricerca Scientifica*, Vol. 9, pp. 10-13 (1938).
- R. J. CASHMAN, "Comments Concerning Anderson's Paper on Contact Difference in Potential between Ba and Mg," *Phys. Rev.*, Vol. 54, p. 971 (1938).
- S. KANEKO, "The Volta Effect between Pure Metals," *Bull. Electrotech. Lab.*, Vol. 2, p. 722 (1938); *Rev. Phys. Chem. Japan*, Vol. 13, p. 59.
- F. A. VICK, "Contact Potentials," *Science Progress*, Vol. 32, pp. 504-9 (1938).
- T. TAKÉUTI, "Contact Potential of Two Electron Gases at Different Magnetic States," *Bull. Tokyo Univ. Eng.*, Vol. 7, pp. 511-12 (1938); *Rev. Phys. Chem. Japan*, Vol. 13, p. 108.
- W. HEINZE, "Contact Potential and Exit-Work," *Zeits. f. Phys.*, Vol. 109, pp. 7-8, 459-71 (1938).

- P. A. ANDERSON, "The Contact Difference of Potential between Ba and Mg," *Phys. Rev.*, Vol. 54, pp. 753-7 (1938).
- P. A. ANDERSON, "The Contact Difference of Potential between Silver Films on Glass and on Rock Salt," *Phys. Rev.*, Vol. 56, p. 850 (1939).
- O. SCARPA, "Volta Effect and the Periodic System of the Elements," *Atti Accad. Lincei*, Vol. 29, pp. 273-6 (1939).
- YU. M. KUSHNIR, E. A. VAINRIB AND V. P. GONCHAROV, "Difference of Contact Potentials between Oxygen-Cesium Surface and Silver," *J. Tech. Phys. (USSR)*, Vol. 9, pp. 2044-7 (1939).
- R. C. L. BOSWORTH, "Contact Potential of Ni," *Trans. Faraday Soc.*, Vol. 35, pp. 397-402 (1939).
- O. SCARPA, "Volta Effect and Electrochemical Potentials," *N. Cimento*, Vol. 17, pp. 54-68 (1940).

## The Theory of Secondary Emission\*

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SEVERAL authors<sup>1,2</sup> have treated the problem of the interaction between energetic primary electrons and the weakly-bound lattice electrons of a solid. However, owing to considerations involving the orthogonality of Bloch wave functions, certain conclusions based upon these theories are incorrect.

The differential cross section for the process in which a primary electron undergoes a transition from a state  $\mathbf{K}$  to a state  $\mathbf{K}'$ , within a solid angle  $d\Omega'$ , is given by

$$d\sigma(\mathbf{K} \rightarrow \mathbf{K}') = \sum_{\mathbf{q}} d\sigma_{\mathbf{q}}, \quad (1)$$

where

$$d\sigma_{\mathbf{q}} = [4m^2 c^4 K' / h^4 S^4 K] \times |\sum_{\mathbf{m}} a_{\mathbf{m}+\mathbf{q}}(\mathbf{k}) a_{\mathbf{m}}^*(\mathbf{k}')|^2 dV'. \quad (2)$$

Here,  $\mathbf{S} = \mathbf{K} - \mathbf{K}'$ ,  $\mathbf{m}$  and  $\mathbf{q}$  are vectors with integer components, and  $\mathbf{k}$  and  $\mathbf{k}'$  are wave vectors corresponding to initial and final states of the lattice electron. The  $a_{\mathbf{m}}$  are the coefficients in the Fourier expansion of the eigenfunctions for a cubic lattice of lattice constant  $a$ .

These have the form

$$\Psi_{\mathbf{k}}(\mathbf{r}) = V^{-1/2} \exp[i\mathbf{k} \cdot \mathbf{r}] \sum_{\mathbf{m}} a_{\mathbf{m}}(\mathbf{k}) \exp[i(2\pi/a)\mathbf{m} \cdot \mathbf{r}]. \quad (3)$$

It is found that for each  $\mathbf{q}$  the following conservation relation holds:

$$\mathbf{S} + \mathbf{k} - \mathbf{k}' + 2\pi\mathbf{q}/a = 0. \quad (4)$$

For given  $\mathbf{K}$ ,  $\mathbf{K}'$ ,  $\mathbf{k}$ , and  $\mathbf{q}$ ,  $\mathbf{k}'$  is uniquely specified by Eq. (4), and the summation indicated in Eq. (1) is equivalent to an integration over final states  $\mathbf{k}'$ .

Because of the presence of  $S^4$  in the denominator of Eq. (2)  $d\sigma_{\mathbf{q}}$  is appreciable only when  $\mathbf{K}'$  has values for which  $S$  is near its minimum  $S_{\min}$ . For primary energies above several hundred eV,  $S_{\min}$  is considerably smaller than any of the other terms in Eq. (4), and, in the region of interest,  $\mathbf{k}'$  is given approximately by

$$\mathbf{k}' \approx \mathbf{k} + 2\pi\mathbf{q}/a. \quad (5)$$

It is consequently assumed for purposes of integration over  $V'$  that  $a_{\mathbf{m}}(\mathbf{k}')$  can be replaced by  $a_{\mathbf{m}}(\mathbf{k} + 2\pi\mathbf{q}/a)$ . This approximation leads to the total cross section of the Wooldridge theory:

$$\sigma_{\mathbf{q}} = \frac{16\pi m^2 c^4}{h^4} \frac{|\sum_{\mathbf{m}} a_{\mathbf{m}+\mathbf{q}}(\mathbf{k}) a_{\mathbf{m}}^*(\mathbf{k} + 2\pi\mathbf{q}/a)|^2}{[(2\pi\mathbf{q}/a) \cdot (2\pi\mathbf{q}/a + 2\mathbf{k})]^2}. \quad (6)$$

However, expressions for secondary yields and energy losses

based upon this cross section actually vanish since, in this approximation,  $\sigma_{\mathbf{q}}$  is zero, a fact not recognized in previous theories. This is an immediate consequence of the orthogonality relation between the lattice eigenfunctions belonging to  $\mathbf{k}$  and  $\mathbf{k} + 2\pi\mathbf{q}/a$ ,

$$\int \psi_{\mathbf{k}} \psi_{\mathbf{k}+2\pi\mathbf{q}/a}^* d\tau = 0. \quad (7)$$

Substitution of Eq. (3) into Eq. (7) yields

$$\begin{aligned} \frac{1}{V} \sum_{\mathbf{m}, \mathbf{n}} a_{\mathbf{n}}(\mathbf{k}) a_{\mathbf{m}}^*(\mathbf{k} + 2\pi\mathbf{q}/a) \int \exp[(2\pi i/a)(\mathbf{n} - \mathbf{q} - \mathbf{m}) \cdot \mathbf{r}] d\tau \\ = \sum_{\mathbf{m}} a_{\mathbf{m}+\mathbf{q}}(\mathbf{k}) a_{\mathbf{m}}^*(\mathbf{k} + 2\pi\mathbf{q}/a) = 0. \end{aligned} \quad (8)$$

Substitution of Eq. (8) into Eq. (6) yields a zero cross section. In order to obtain a finite result, it is necessary to take into account the variation of  $a_{\mathbf{m}}(\mathbf{k}')$  with  $\mathbf{K}'$ . This can be accomplished by a Taylor series expansion of  $a_{\mathbf{m}}(\mathbf{k}')$  about the point  $\mathbf{k}' = \mathbf{k} + 2\pi\mathbf{q}/a$ . This results in a cross section which for sufficiently high energies has the same form as that obtained by Bethe<sup>3</sup> for the ionization of atoms, namely,

$$\sigma_{\mathbf{q}} = (A/E) \ln(E/E'), \quad (9)$$

where  $E$  is the energy of the primary electron and  $A$  and  $E'$  are parameters characteristic of the medium. A similar expression is obtained for the rate of energy loss by electrons passing through solids. These results are entirely different from those obtained on the basis of Eq. (4), which have previously been interpreted<sup>1,2</sup> to mean that both the rate of production of secondaries and the rate of energy loss should be practically independent of the energy of the primary. Actually, these quantities are zero in the approximation leading to Eq. (4), and as indicated by Eq. (9) and the equivalent expression for the energy loss, they decrease rapidly with energy.

It should be pointed out that the above considerations do not apply to the case of free electrons ( $\mathbf{q} = 0$ ), which has been treated by Baroody<sup>4</sup> and by Dekker and van der Ziel<sup>5</sup>, since values of  $\mathbf{S}$  in the neighborhood of  $S_{\min}$  are forbidden because they correspond to transitions to occupied states.

The questions outlined here will be treated in more detail in a forthcoming paper.

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<sup>1</sup> D. E. Wooldridge, Phys. Rev. **56**, 562 (1939).

<sup>2</sup> A. J. Dekker and A. van der Ziel, Phys. Rev. **86**, 755 (1952).

<sup>3</sup> H. Bethe, Ann. phys. **5**, 325 (1930).

<sup>4</sup> E. M. Baroody, Phys. Rev. **78**, 780 (1950).

# Fundamentals of Secondary Electron Emission\*

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**Summary**—Secondary electron emission is of great importance to the physicist because of its bearing upon the problem of the interactions between fundamental particles and to the radio engineer because of its applications, as well as its effect, upon the operation of electronic tubes. A complete theoretical picture capable of accounting quantitatively for all observed phenomena does not exist. Secondary electron emission differs from other modes of emission in many respects. The essential characteristics can best be evaluated by considering a typical experimental arrangement for investigating the phenomenon. Three categories of emitted electrons are recognized. The yield may depend upon various factors, such as the primary energy, collector voltage, target temperature, time, angle of incidence, atomic properties of target, and the composition of the target.

The difficulties of propounding a satisfactory theory are evident from an individual consideration of each of the various processes involved. The primary interaction, primary energy loss, escape of secondaries, and integration over the range of the primary must each be treated to arrive at a final solution. In several previous attempts at formulating a theory, only the most loosely bound electrons in the solid have been regarded as constituting the source of secondary electrons. Normalizations are required for comparison of the results with existing experimental data. There are cogent reasons for regarding bound electrons as a very important source of secondaries. The probability of ionization in gases exhibits the same general dependence upon primary energy as secondary electron emission, and this resemblance suggests a possible model for secondary emission based upon detailed considerations of primary ionization probabilities.

## I. INTRODUCTION

WHEN A SOLID BODY is subjected to bombardment by electrically charged particles, some electrons which may be detectable under suitable circumstances are always emitted. Although this process, commonly designated "secondary electron

emission," has been observed to occur in various forms, by far the most widely investigated type is that in which an electron beam falling upon the surface of a target in a vacuum causes the emission of a stream of electrons from the surface upon which it impinges. It should be emphasized, however, that this variety of secondary emission is not endowed with any intrinsically greater significance than any other. Rather, the distinction arises solely from the geometrical and practical circumstances that in this case the phenomenon is readily observable and is, in fact, involved in the operation of common electronic devices.

In the field of radio engineering, secondary electron emission originally manifested itself only as a source of annoyance which seriously interfered with the satisfactory functioning of vacuum tubes. The problem was solved by the addition of the suppressor grid or its equivalent to the tetrode; after the advent of the pentode, the effect received relatively little attention. In recent years, however, successful attempts, both unintentional and conscious, have been made to utilize the phenomenon to some advantage. It is now generally realized that secondary electron emission is inherent in the operation of a cathode-ray tube. Devices such as the magnetron and certain types of reflex klystron depend upon secondary electron emission for their high output capabilities. In dynatron and photomultiplier tubes, secondary electron emission constitutes the fundamental principle of operation.

Electron emission may be divided into four principal categories: (1) thermionic emission, (2) photoelectric emission, (3) field emission, and (4) secondary emission. Despite the radical differences among these modes of emission, certain similarities exist among the first three. In general, satisfactory theories have been formulated (although complicated systems, such as activated

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barium-strontium oxide-coated cathodes, have been the subject of considerable controversy) despite the fact that they may be unable to account for all observed phenomena quantitatively (as in the case of the photoelectric effect). Nothing resembling a complete theoretical picture of secondary electron emission exists up to the present time, nor is it likely that an all-inclusive model can be developed in the light of the limitations of our present grasp of physics of the solid state.

The most striking characteristic of secondary emission as contrasted with the other types is the similarity of behavior over a wide variety of materials. The range of values of yields encountered is quite limited as compared with thermionic or photoelectric yields. The nature of the dependence of secondary emission upon the work function of the surface differs appreciably from that in the other cases, and the yield is actually quite insensitive to the nature of the barrier. At first sight it might be expected that secondary emission is more closely related to photoelectric emission than to thermionic emission. This resemblance, which happens to be valid in a certain sense for rather subtle reasons, cannot be accorded much significance upon closer scrutiny. Whereas photoelectric emission from a solid is primarily a surface effect, this is certainly not the case for secondary emission. A single photoelectron absorbs all of the energy of the incident quantum  $h\nu$ , and hence the situation is dominated by the work function  $\phi$ . On the other hand, each secondary electron absorbs only a small fraction of the energy of the primary which may penetrate a considerable distance into the target material. Thus, we are here concerned with a combination of volume and surface effects.

From the standpoint of tube engineering, the operational problems associated with secondary electron emitters are to some extent somewhat less complicated than those encountered in applications utilizing thermionic emission. It is appropriate to emphasize at this time that the generalizations to which the discussion in this paper will be confined are occasionally subject to exceptions. In the event that these are not specifically mentioned, it should not be tacitly assumed that the broad statements are necessarily all-inclusive. For example, there are certain specific applications for which the requirements of reproducibility and long-time stability of specially prepared targets present very difficult technical problems. Except for a few composite surfaces with certain desired characteristics, activation procedures are not involved. As in the case of thermionic emitters, there are two general classes of materials which are useful as a source of electrons, namely, metals and semiconductors. A third class, broadly termed "insulators" for lack of a less ambiguous designation (note that semiconductors under some conditions are included in this group), is also of importance primarily because of practical applications, although the first two present greater theoretical interest.

## II. BASIC EXPERIMENTAL CONCEPTS

The most direct approach to an evaluation of the significant characteristics of secondary electron emission is to consider a typical experimental arrangement for investigating this phenomenon. Fig. 1 is a schematic

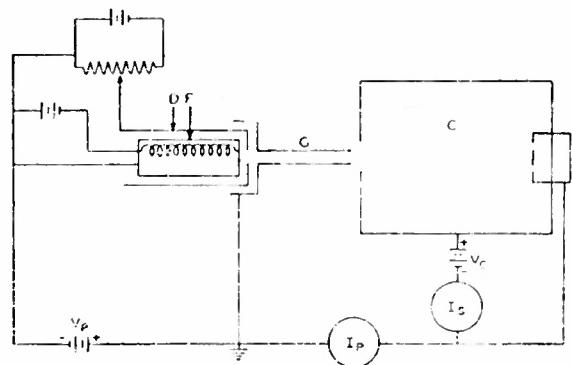


Fig. 1—Schematic diagram of a typical experimental arrangement for measuring secondary electron emission.

diagram of such an apparatus. It consists essentially of an electron gun  $G$  serving as the source of a beam of primary electrons  $I_p$  which, after acceleration through a difference of potential  $V_p$ , bombards the target  $T$ . The secondary electrons  $I_s$  leaving the target are then attracted to the collector  $C$ , owing to the presence of the positive voltage  $V_c$  applied to the collector with respect to the target.

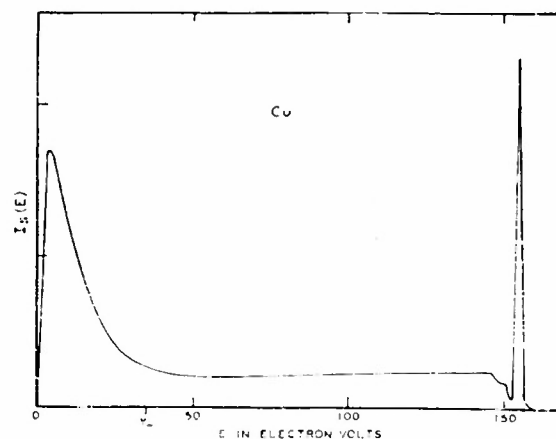


Fig. 2—Typical energy distribution of secondary electrons. This particular curve, obtained by a method utilizing a transverse magnetic analyzer, refers to a Cu target. (See E. Rudberg, *Phys. Rev.*, vol. 50, p. 138; 1936.)

The yield  $\delta$  is defined as the number of secondaries collected per incident primary, given by the ratio  $I_s/I_p$ . It should be noted that this is a purely empirical definition, but nevertheless one of practical interest in any event. Some of the primary electrons are directly reflected, whereas others are scattered with some loss of



energy. These do not constitute true secondary electrons which have actually been knocked out of the target by an impinging primary. It is practically impossible to distinguish between true secondaries and primaries reflected after suffering energy losses, and this is indeed unfortunate from the point of view of obtaining theoretically useful experimental data. However, the distinction is unnecessary as regards obtaining "emission" from a target regardless of the origin of the "emitted" electrons.

It has been stated that the secondary electrons emitted by a material bombarded by a primary beam can be ascribed to three different mechanisms. This classification is made on the basis of the energy distribution of collected electrons, which is obtained by applying retarding potentials  $-V_r$  to the collector with respect to the target, taking into account the contact difference in potential between the surfaces of these two electrodes. As is evident in Fig. 2, there is a sharp distinguishable peak at the energy of the incident beam corresponding to  $eV_p$ , and these electrons are, of course, to be identified as elastically reflected primaries. At the other end of the spectrum a group of slow electrons may be observed. The average energy of these electrons is only a few ev when the primary energy is of the order of hundreds of ev. Between these electrons and the elastically reflected primaries there is an intermediate group which results principally from inelastic scattering in the lattice. The slow electrons arise from collisions between the primaries and the atomic electrons of the target in which sufficient energy is transferred to the latter so that they can penetrate to the surface and emerge from the solid material. These electrons are therefore true secondaries; although most possess low energy, it is certainly not warranted, however tempting, to assign an arbitrary upper limit, such as  $V_A$ , above which no true secondaries appear and below which scattered primaries are prohibited.

Various factors in addition to the nature of the target material may affect the magnitude of the yield of secondary electrons. These will be discussed briefly in a general manner, and certain special situations will be mentioned.

#### A. Primary Voltage $V_p$

All known secondary emitters manifest the same qualitative dependence of yield upon primary energy. Starting at low voltage, the yield rises smoothly until a maximum value, often in the neighborhood of 400 to 600 volts, is attained. Thereafter, the yield decreases slowly and may approach a more or less constant value at very high energy. A typical curve is shown in Fig. 3. The maximum value of the yield,  $\delta_{\max}$ , is often cited, probably because it is convenient, at least from the practical point of view and for some purposes, to know the highest multiplication which could be expected under optimum conditions. The corresponding voltage is design-

ated  $V_{p\max}$ . Although  $\delta_{\max}$  and  $V_{p\max}$  alone are not necessarily of any fundamental theoretical significance, it is interesting that at least in the case of metals a universal curve which fits the available data within the experimental errors is obtained by applying a

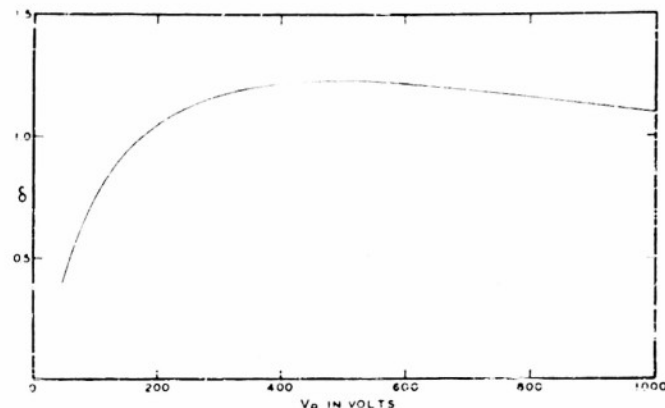


Fig. 3—Dependence of secondary electron emission upon primary bombarding energy for a typical metal, in this case Ni.

normalization in which the ratio  $\delta/\delta_{\max}$  is plotted as a function of  $V_p/V_{p\max}$ . This is shown in Fig. 4. The shape of the *yield versus energy* relationship can be accounted for, at least qualitatively, as will be described in the following section.

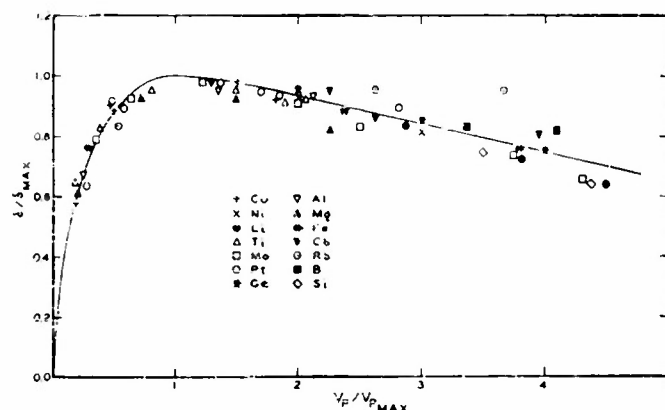


Fig. 4—Normalized yield,  $\delta/\delta_{\max}$ , plotted as a function of normalized primary energy,  $V_p/V_{p\max}$ , for various elements. This is the so-called universal curve of secondary electron emission.

Other values of primary voltage sometimes cited because of practical considerations, particularly in the case of insulators, are the two crossover points, in the  $\delta$  versus  $V_p$  plot, at which the yield attains the value unity. It is evident that if an insulator is subjected to electron bombardment the surface will charge negatively, as long as the yield is less than one secondary per incident primary, until it approaches the cathode

potential, thereby effectively reducing the primary bombarding energy. When the yield exceeds unity, between the so-called "lower and upper sticking potentials" a positive charge is acquired by the surface, thereby reducing the effective collector voltage  $V_c$  until the measured yield approaches one. Above the upper crossover voltage, the surface becomes negatively charged until the yield again approaches unity.

### B. Collector Voltage $V_c$

In the case of metals, the secondary current is independent of the collector voltage as long as this is positive. For substances with lower conductivity, such as certain oxides, on the contrary, an increase of yield with increasing collector voltage is sometimes observed,

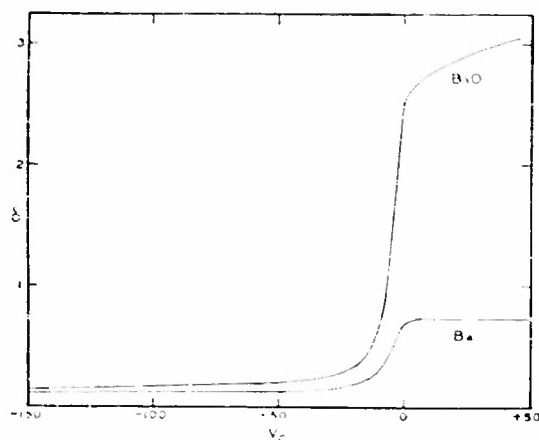


Fig. 5—Dependence of yield upon collector voltage, illustrating lack of saturation<sup>1</sup> in the case of BaO. (See H. Bruining and J. H. De Boer, *Physica* (The Hague), vol. 6, p. 823; 1939.)

as is illustrated in Fig. 5. This effect may be qualitatively understood when it is recognized that by virtue of a yield larger than unity more electrons leave the emitter than enter. As a consequence of the high resistance of the oxide layer, a positive charge will appear on the outer surface and a negative charge on the inner surface, thereby forming a double layer. The resulting field promotes a phenomenon analogous to cold emission. The dependence upon collector voltage arises from the fact that the potential on the outer surface of the oxide layer is limited to values smaller than the collector voltage. An increase in the latter is accompanied by an increase in the internal field.

### C. Temperature of Target

The secondary electron emission from metallic materials is not ostensibly dependent upon the temperature of the target, at least in any fundamental manner. Actually, changes in the nature of the surface layer or in the crystal structure may be introduced by heat treatment, thereby producing only small changes in secondary emission. In the case of at least one semiconducting medium, which in particular has been investigated rather extensively because of its great practical im-

portance—the so-called oxide-coated cathode—, appreciable variations with temperature do occur.<sup>1,2</sup>

### D. Time

At least in the case of metals, there are no essential changes of secondary electron emission with time, except for obvious consequences of structural changes which the target surface may undergo during the lifetime of the tube. Specialized emitters consisting, for example, of thin films of aluminum oxide on an aluminum base, with an outer layer of Cs, operating by virtue of the so-called "Maltzer Effect,"<sup>3</sup> are capable of emitting thousands of electrons per bombarding primary. This phenomenon, also termed "thin-film field emission," is produced by an extreme manifestation of the mechanism already described in Section II B. It is evident that it might be anticipated from the nature of the process that the maximum emission is not attained until the primary beam has been on for some time and, furthermore, that emission may persist after the beam has been turned off; this is quite contrary to the situation with ordinary secondary electron emission which displays no detectable time delays.

### E. Angle of Incidence

The data plotted in Fig. 3 were obtained with the beam striking the target surface perpendicularly. As might be expected from the general nature of the processes involved, the yields for oblique incidence are somewhat larger inasmuch as the secondary electrons are formed closer to the surface and are consequently absorbed to a lesser extent before reaching the surface barrier.

For nearly grazing incidence, the yield may be increased by a factor of as much as three, depending upon the primary voltage and the composition of the target. In general, the maximum value of the yield and the energy at which it occurs are both higher, which is consistent at least with qualitative expectations.

### F. Atomic Properties of Target

No simple correlation between the secondary yield and the known atomic properties of the target exists, as in the case of other types of electron emission. In some instances, trends which are certainly suggestive are revealed, although the relationships are evidently indirect. For example, the curve in Fig. 6 shows the correlation between  $\delta_{max}$  and  $\phi$ . The positive slope is opposite that which would be expected at first sight, and the suggestion of a correlation is a consequence of the fact that the work function changes along with some other atomic property which really predominates the second-

<sup>1</sup> M. A. Pomerantz, "Secondary electron emission from oxide-coated cathodes," *Jour. Frank. Inst.*, vol. 241, p. 415; vol. 242, p. 41; 1946.

<sup>2</sup> J. B. Johnson, "Secondary electron emission from targets of barium-strontium oxide," *Phys. Rev.*, vol. 73, p. 1058; 1948.

<sup>3</sup> L. Maltzer, "Thin-film field emission," *Phys. Rev.*, vol. 50, p. 48; 1936.

ary emission process. Actually, a reduction in  $\phi$ , introduced without alteration of the bulk material, would result in an increase in the yield.

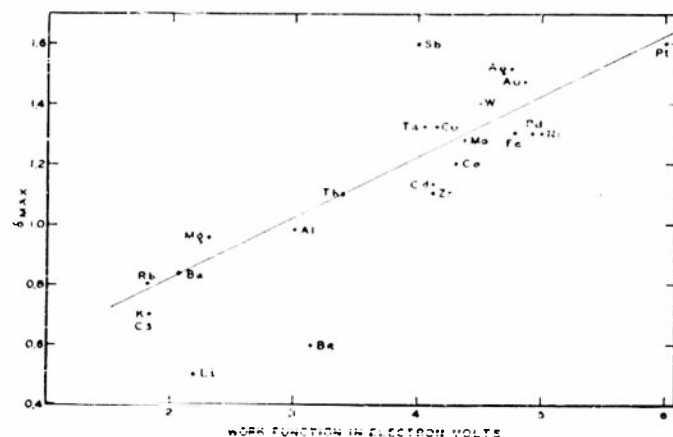


Fig. 6—Correlation between maximum secondary electron emission and work function for various metals.<sup>14</sup>

Another illustration of the sort of trend which may be exhibited is shown in Fig. 7, where the yield is plotted as a function of the first atomic ionization potential of the target element. Now obviously, this characteristic itself retains no significance when the atoms are brought together to form a solid. However, it is not unreasonable to assume that it may reflect the effective number of conduction electrons in the metal (high-ionization potentials corresponding to small effective numbers) and hence the number of electrons which will impede the progress of an outgoing secondary. Thus, the addition of an electron to the outer shell should decrease the yield. It has not yet been possible to test this hypothesis experimentally because of the inavailability of the requisite data.

### G. Composition of Target

It was noted in the introduction that secondary electron emission is unique as contrasted with the other types, in view of the relative insensitivity to the nature of the emitting material. It is indeed remarkable that values of  $\delta_{\max}$  (including special unstable cases of high yields) vary only by a factor somewhat greater than one order of magnitude. It is appropriate to include herewith at least a general statement regarding the values of yield which are encountered in practice.

Secondary electron emitters may be classified into four categories as follows:

(1) Elements: This group includes all chemical elements normally in the solid state for which measurements have been reported. The maximum values of the yield range from about 0.5 to 1.6 for clean surfaces, regardless of the specific nature of the conductivity of the solid.

(2) Compounds: This group includes all chemical

compounds which are designated either as semiconductors or as insulators at room temperature. The maximum values of the yield range from approximately 1.0 to 7.5.

(3) Composite surfaces: These are various complicated systems, sometimes designated "photocathodes" because they are characterized by very high photoelectric sensitivity, usually prepared by evaporating layer upon layer of different materials in a vacuum and by performing other special operations. For example, the notation  $[\text{Ag}]-\text{Cs}_2\text{O}$ ,  $\text{Ag}-\text{Cs}$  refers to an electrode consisting of a silver base covered with a  $\text{Cs}_2\text{O}$  layer (also containing Ag atoms), on the surface of which Cs atoms are absorbed. The yields range between 3 and 10, in general.

(4) Activated alloys: Certain alloys, for example several per cent Mg with Ag, when "activated" by what appears to be an oxidation procedure, produce yields as high as 18, without any stability. Yields as high as 4 to 5 can be maintained.

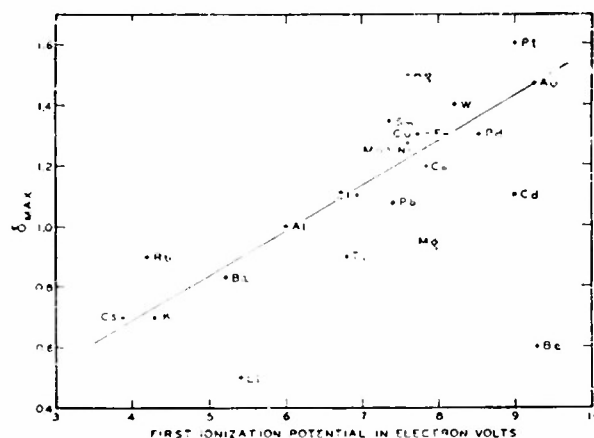


Fig. 7—Correlation between maximum secondary electron emission and first atomic ionization potential for various elements.

## III. THEORY OF SECONDARY EMISSION

In contrast to the theory of thermionic emission, the theory of secondary emission is in a very unsatisfactory state. This is a consequence of the fact that whereas the problem of thermionic emission can be treated in a fairly straightforward manner by standard techniques of statistical mechanics<sup>4</sup> that of secondary emission is highly complex, involving several processes none of which is well understood. The difficulties involved become obvious from an examination of the following outline which lists the steps in the computation of the secondary yield from a solid.

### A. The Primary Interaction

The problem here is to compute the probability that a primary electron of a given energy will interact with one of the electrons in the solid to produce a sec-

<sup>14</sup> K. G. McKay, "Advances in Electronics," Academic Press, Inc., New York, N. Y., vol. 1; 1948.

<sup>4</sup> W. E. Danforth, "Elements of thermionics," *Proc. I.R.E.*, vol. 39, p. 485; May, 1951.

ondary electron with sufficient energy to emerge. Our present state of knowledge of solids is such that it is certainly impossible to solve even this very fundamental problem in any exact way. It is not even clear, for example, whether the sources of secondary electrons in a metal are the conduction electrons or the more tightly bound inner-shell electrons, a complication that does not exist in thermionic emission since it is known in that case that only the conduction electrons can be involved. Any attempt to discuss the question of primary interaction thus involves the introduction of certain simplifying assumptions about the solid, and even then the problem is generally extremely complicated.

### B. Primary Energy Loss

The probability of producing a secondary electron of a given energy certainly depends upon the energy of the primary that produces it. Consequently, one must have some knowledge of the energy of the primary as a function of the depth to which it has penetrated. Since there is no experimental evidence available on the rate of energy loss of low-energy primaries, it must be computed theoretically. Inasmuch as the primary can lose energy in several ways (production of secondaries, excitation of bound electrons, and the like), such a computation is very difficult.

### C. Escape of Secondaries

In order for a secondary to be observed, it must escape from the surface of the solid. To accomplish this, it must move through the body of the solid from the point at which it was created to the surface, retaining sufficient energy to penetrate the surface potential barrier. Although the problem of the penetration of the barrier can be treated quite adequately, the motion of a slow secondary through the solid is not at all well understood. Several possible assumptions can be made, such as exponential absorption, random diffusion, uniform energy loss, and the like, but whether any of these assumptions are valid is not at all clear.

### D. Integration over the Range of the Primary

The solution of the above problems will furnish information regarding the number of emergent secondaries which are produced at a given depth in the solid. In order to obtain the total yield, it is necessary to integrate this result over all possible depths, i.e., from zero to the total range of the primary. If steps (A), (B), and (C) have been solved, this process can always be accomplished numerically if necessary, and consequently this does not represent an essential difficulty.

As may be concluded from the above discussion, the general problem of secondary emission is very complicated, and at present the only feasible approach involves adopting various simplifying assumptions and investigating the agreement between theories based on these approximations and experiment. Several theories of secondary emission from metals have been developed

in this manner. Of these we shall discuss the theories of Baroody and Wooldridge which, though not the only attempts, are quite typical of the usual approach, since both assume that the loosely bound valence electrons constitute the principal source of secondaries.

Baroody's theory,<sup>5</sup> which is somewhat simpler, employs the Sommerfeld model of the metal, as is done in the theory of thermionic emission. The interaction between the primary and secondary electrons is treated in a purely classical manner, and the secondaries are assumed to be absorbed exponentially in their passage to the surface. This theory, in common with all existing theories of secondary emission, involves several parameters whose magnitudes are unknown, and consequently the values of the secondary yields to be expected from metals cannot be computed in absolute terms. A relation between yield and energy is obtained, however. Baroody points out the existence of the universal curve shown in Fig. 4, relating experimental values of the secondary yield and energy, and compares his theoretical results with it. Unfortunately, although the theoretical curves have the same general form, the quantitative agreement is very poor. For example, for  $V_p/V_{pmax} = 4.5$ , the experimental value of  $\delta/\delta_{max}$  is three times the computed value. This lack of agreement should not cause great concern, however, inasmuch as this application of the Fermi gas model is exceedingly questionable, and the aim of the investigation was primarily to demonstrate certain qualitative features of secondary emission.

Wooldridge's theory<sup>6</sup> is similar to Baroody's in that it considers only the valence electrons as potential secondary electrons, and assumes an exponential law for their absorption. It differs from Baroody's theory in treating the primary interaction quantum mechanically and taking into account the interaction of the valence electrons with the lattice. Again, absolute values of yields cannot be determined, and for comparison with experiment, the theoretical value of  $\delta_{max}$  is set equal to the empirical value. Within the expected range of validity of the formulas, the yield curves thus obtained agree with experiment quite well for the dense metals, such as silver and copper; but for less dense substances, such as lithium and aluminum, the agreement is rather poor. Wooldridge assumes that the primary loses energy only by the production of secondaries, and attributes the disparity with experiment in the case of light elements to the neglect of other types of energy loss. It is quite possible, however, that this disagreement arises from errors inherent in the basic assumptions.

Both of the aforementioned theories are based upon the hypothesis that valence electrons are the principal source of secondaries, and at sufficiently low primary

<sup>5</sup> E. M. Baroody, "A theory of secondary electron emission from metals," *Phys. Rev.*, vol. 78, p. 780; 1950.

<sup>6</sup> D. E. Wooldridge, "Theory of secondary emission," *Phys. Rev.*, vol. 56, p. 562; 1949.

energies, this is undoubtedly the case. At very high primary energy, on the other hand, bound inner-shell electrons are the principal source since their binding is then very small compared to the energy of the incident primary and since they are much more numerous than the valence electrons. At intermediate energies (approximately 100 to 2,000 volts) it is not at all obvious that one group of electrons or the other necessarily plays the dominant role. The work of Baroody, Woolridge, and others shows that by proper choice of parameters, the yield versus energy curves for metals can be explained qualitatively on the valence electron assumption, and for some metals, as mentioned above, good quantitative agreement is even obtained.

The hypothesis that the bound electrons may be the principal source of secondaries has not as yet been investigated quantitatively; however, there are cogent qualitative arguments indicating that this may be the case. (1) Bound electrons which could be available as secondaries are much more numerous than the valence electrons in most metals. (2) The ionization of gases has been investigated experimentally, and it has many features in common with secondary emission from metals. In particular, if the probability of ionization  $\sigma$  of a gas molecule is plotted as a function of the energy  $W$  of the incident electron, a curve having the same general form as the secondary yield curve shown in Fig. 3 is obtained. Furthermore, if this curve is normalized by plotting  $\sigma/\sigma_{\max}$  against  $W/W_{\max}$ , a universal curve which is very similar to the universal emission curve results, as is seen in Fig. 8.

This resemblance suggests a possible model for secondary emission. If the bound electrons in a solid are the principal source of secondaries, the production of an internal secondary will be essentially an ionization process. Hence the probability of production should have much the same dependence on energy as the probability of ionization of gases. Although many factors affect the shape of the secondary yield versus energy relationship, it is quite possible that the primary interaction is the dominant factor, in which case the universal secondary emission curve and the universal ionization curve should be very similar. An examination of Fig. 8 reveals that this is indeed the case. Furthermore, rough calculations indicate that if one modifies the gas curve to take into account the fact that only those electrons with sufficient energy to penetrate the surface barrier can be observed as secondaries, the resultant curve will be in even better agreement with the secondary emission curve.

Consequently, it seems important to investigate in more detail the possibility that the bound electrons may be an important source of secondaries. It should be pointed out that whether or not the conduction electrons in a metal are a copious source of secondaries they are certainly of great importance in the emission process since it is very likely that interactions between internal secondaries and the conduction electrons are

responsible for most of the secondary absorption which so drastically limits the secondary yield of metals. It might be expected that, in the case of metals, filling an inner-shell in progressing through the periodic system should increase the secondary electron emission, whereas the addition of an electron to the outer-shell should decrease the yield. The absence of conduction electrons in insulators thus accounts for their high secondary yields.

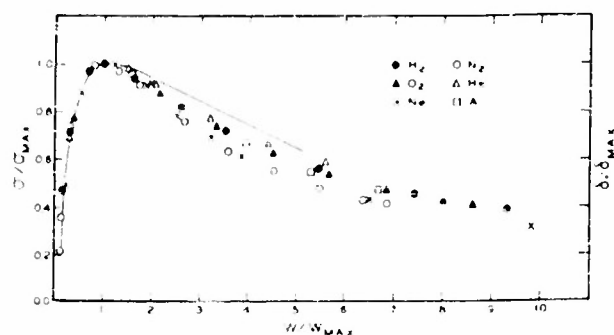


Fig. 8—Normalized primary ionization probabilities,  $\sigma/\sigma_{\max}$ ; plotted as a function of normalized primary energy,  $W/W_{\max}$ , for various gases. The solid curve is the universal curve of secondary electron shown in Fig. 4.

#### IV. CONCLUSION

Many specialized features of secondary electron emission have not been mentioned in this paper, and it has been possible to include only a brief summary of the salient features of the phenomenon, in conformity with the primary purpose of this review. Frequent references and inclusion of detailed descriptions of experiments have necessarily been avoided in the interests of stressing general principles rather than presenting an encyclopedic survey of the literature. For this reason, descriptions of applications of the phenomenon have likewise been omitted. For additional facts, the reader is referred to the lengthier articles containing rather comprehensive bibliographies.<sup>7,8</sup>

In conclusion it seems appropriate to hazard a prediction regarding the course of future progress in this field. Certainly the known engineering goals are well defined; efforts to obtain high yields with good stability will undoubtedly be continued, together with the search for new applications of the effect. From the scientific point of view, there is need for a self-consistent series of reliable measurements on all chemical elements in the periodic system which can be made into suitable targets. The disagreement among the results of different experiments is such as to preclude many crucial comparisons which could cast light upon the nature of the mechanisms involved in the process of secondary emission.

<sup>7</sup> K. G. McKay, "Advances in Electronics," Academic Press, Inc., New York, N. Y., vol. I, 1948.

<sup>8</sup> H. Bräunig, "Die Sekundär-Elektronen-Emission fester Körper," Julius Springer, Berlin, 1948.



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